Bridged Ring Systems Containing Phosphorus: Structural Influences on the Stereochemistry of Silane Reductions of *P*-Oxides and on ^{13}C and ^{31}P NMR Properties of Phosphines[1]

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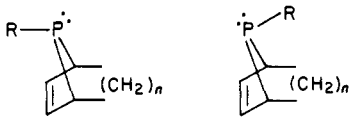
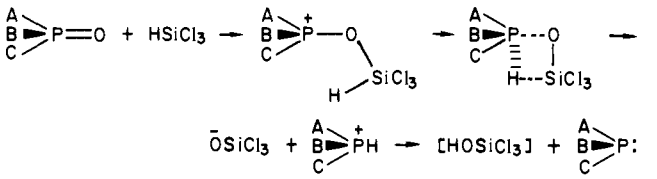
Abstract: A number of bridged cyclic phosphine oxides, both saturated and unsaturated, have been reduced with silicon-based reagents. Evidence was obtained that pentacoordinate intermediates can have special importance in such reductions, since the contracted angle in the cycle is more compatible with the 90° angle offered by apical–equatorial bonding in the trigonal bipyramid. Thus, while $HSiCl_3$ and $C_6H_5SiH_3$ reduce noncyclic oxides with stereochemical retention, phosphines with either retained or inverted configuration can result from angle-contracted, cyclic oxides, and in the 7-phosphanorbornene system (but not in higher homologues) the P(III) intermediate can undergo retrocycloaddition, causing loss of the phosphorus bridge. However, when the pyridine complex of $HSiCl_3$ is used, these complications are avoided, apparently because of a change in mechanism. The bridged phosphines have been characterized by ^{13}C NMR spectroscopy, which is especially useful in revealing stereochemical features and modifications in the hybridization at phosphorus. Angle contraction in the ring diverts s-character into the exocyclic bond, causing extremely large $^1J_{PC}$ values. Syn,anti isomers then appear to have different hybridization as judged by variations in their $^1J_{PC}$ values. ^{31}P NMR chemical shifts occur far downfield in 7-phosphanorbornenes, apparently as a result of $\sigma-\pi$ hyperconjugation; the anti isomer experiences a second effect, tentatively attributed to repulsion of the lone pair by interaction with the π-electrons, which superimposes shielding on ^{31}P and causes their shifts to be significantly upfield of the syn isomers. The downfield shifting is weaker in 8-phosphabicyclo[3.2.1]octenes and absent in the [4.2.1] homologue. Saturated strained phosphines have shifts in the range of acyclic compounds. In two diphosphines, P–P coupling is present and its magnitude shown to be controlled by the orientation of the lone pair on phosphorus.

The placement of phosphorus in heterocyclic frameworks can cause some important modifications in the properties associated with the particular phosphorus functionality.[2] This is especially true when the creation of the cyclic structure requires strong contraction of the bond angles around the phosphorus atom, as in bridged ring systems. In working with tertiary phosphines and phosphine oxides containing this structural feature, we have encountered unique features in their reaction chemistry and NMR spectral properties. In this paper attention is focused on the stereochemical aspects of the highly important deoxygenation of phosphine oxides by silicon hydrides,[3] which is generally the principal method by which phosphines with bridged rings are approached. While not a systematic study, our research has gathered enough information to show that serious departures from the mechanistic and stereochemical pathways established for simpler compounds can occur when phenylsilane and trichlorosilane are used as the reducing agents. Two configurations are usually possible for phosphines in bridged structures, and it is frequently found[4,5] that steric effects cause striking differences in both the ^{13}C and the ^{31}P NMR chemical shifts and coupling constants of the isomers. This is especially true where environments on either side of the phosphorus bridge are greatly dissimilar, as in syn,anti isomers such as **1a** and **1b** (n = 2 or 3).



1a syn **1b** anti

Scheme I



The deoxygenation of phosphine oxides, a reaction of paramount importance in synthetic organophosphorus chemistry, is generally accomplished with silicon hydrides[6] or hexachlorodisilane.[7] In stereochemical studies of these processes, it was shown[8] that trichlorosilane reduced optically active acyclic phosphine oxides largely with retention of configuration, and later it was established that retention was also the exclusive result with phenylsilane[9] in a study that also included simple heterocyclic compounds.[10] To accommodate this stereochemical result, both groups[8,9] proposed that the deoxygenation occurred without the formation of a pentacoordinate, trigonal-bipyramidal (TBP) intermediate, since isomerization of TBP structures is a well-known, low-energy process that could lead to the product of inversion. Instead they proposed that a four-center intramolecular mechanism (exemplified in Scheme I for $HSiCl_3$) was operative, so that H could be transferred to P from Si at the face from which oxygen departed, thereby preserving the configuration.

The occurrence of some inversion in $HSiCl_3$ reductions, however, may suggest some involvement of a pentacovalent intermediate.[11] The four-center mechanisms are generally accepted today,[12] although it is now known[13] that when amines with the basicity of

(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Taken in part from the doctoral dissertations of K.A.M. (1980) and K.C.C. (1983).

(2) Quin, L. D. "The Heterocyclic Chemistry of Phosphorus"; Wiley-Interscience: New York, 1981.

(3) For recent summaries of the scope of these reactions, see: (a) Weber, W. P. "Silicon Reagents for Organic Synthesis"; Springer-Verlag: Berlin, 1983. (b) Elsner, G. In "Methoden der Organischen Chemie (Houben-Weyl)", 4th ed.; Regitz, M., Ed.; Georg Thieme Verlag: Stuttgart, 1982; Vol. E1, pp 165–167.

(4) (a) Quin, L. D.; Mesch, K. A. *J. Chem. Soc., Chem. Commun.* **1980**, 959. (b) Mathey, F.; Mercier, F. *Tetrahedron Lett.* **1981**, 319.

(5) Marchand, A. P. "Stereochemical Applications of NMR Studies in Rigid Bicyclic System"; Verlag Chemie: Deerfield Beach, FL, 1982.

(6) Fritzsche, H.; Hasserodt, U.; Korte, F. *Chem. Ber.* **1964**, *97*, 1988.

(7) Naumann, K.; Zon, G.; Mislow, K. *J. Am. Chem. Soc.* **1969**, *91*, 2788.

(8) Horner, L.; Balzer, W. D. *Tetrahedron Lett.* **1965**, 1157.

(9) Marsi, K. L. *J. Org. Chem.* **1974**, *39*, 265.

(10) A later report from another laboratory stated that some inversion occurred with certain phosphetane oxides: Oram, R. K.; Trippett, S. *J. Chem. Soc., Perkin Trans. 1* **1973**, 1300.

(11) Luckenbach, R. "Dynamic Stereochemistry of Pentacoordinated Phosphorus and Related Elements"; Georg Thieme Verlag: Stuttgart, 1973; p 11.

(12) Goldwhite, H. "Introduction to Phosphorus Chemistry"; Cambridge University Press: Cambridge, 1981; p 71.

(13) Naumann, K.; Zon, G.; Mislow, K. *J. Am. Chem. Soc.* **1969**, *91*, 7012.

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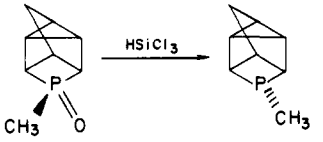
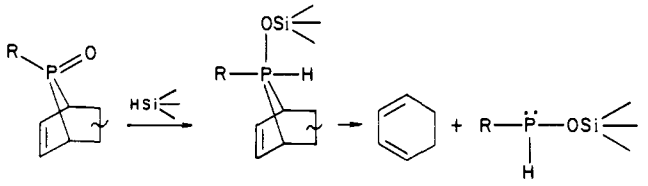
triethylamine are present the reduction follows a quite different course, involving a pentacoordinate intermediate $R_3P(SiCl_3)(OSiCl_3)$, and gives predominantly the inverted product. Weaker bases such as pyridine form complexes with trichlorosilane, but do not alter the stereochemical result of retention, and therefore these reductions are presumed not to proceed through P(V) intermediates. Even when an example[14] of complete inversion was encountered in the trichlorosilane reduction of phosphine oxide **2**, the reaction was still assumed to occur with retention, but HCl in the medium was proposed to cause the inversion.



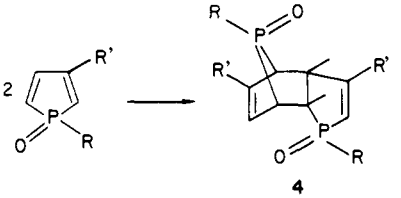
2 **3**

We will show in this paper that, when the phosphine oxide is incorporated in a strained bridged structure, it is not uncommon for inversion to occur on phenylsilane and trichlorosilane reductions, and consequently one must be cautious in assigning stereochemistry to the phosphines in the absence of confirming spectral evidence. We shall also show that, in cases where trichlorosilane reduction gives an inverted product, the addition of pyridine to the medium causes a return to the common result of retention. To explain these abnormal stereochemical results in bridged systems, we will postulate that relief of strain encourages a true pentacovalent intermediate to develop; polytopal isomerization of the TBP occurs before breakdown of the P(V) form, and thus isomeric phosphines are produced. Evidence for the P(V) intermediate can in some cases be found in the occurrence of a side reaction, a fragmentation of the intermediate by a retrocycloaddition process. This is a common event in the 7-phosphanorbornene system and can be described as a retro-McCormack reaction.



The forward process, reacting dienes and P(III) halides, is a fundamental synthetic method of phosphorus chemistry,[2] but it has not been successful with cyclohexadienes. Other examples of retro-McCormack reactions are known; the dioxyphosphoranes formed from 3-phospholenes with dialkyl peroxides[15] or α-dicarbonyl compounds[16] fragment readily by this process.

Reduction of Strained Phosphine Oxides. 7-Phosphanorbornene Derivatives. The dimers of phosphole oxides, easily obtained[17] and characterized spectrally,[18] are useful as model 7-phosphanorbornene derivatives. The dimerization is stereospecific.[18,19]



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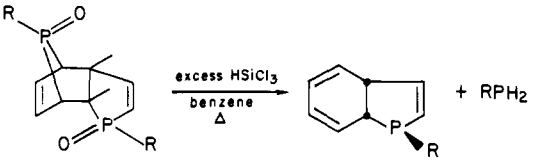
When the dimer (**5**) of 1-methylphosphole oxide was reacted with excess trichlorosilane under the conventional conditions of refluxing a benzene solution for 1–2 h, no product with retention of the molecular framework could be detected. The phosphorus bridge was expelled and converted to CH_3PH_2, and a 3a,7a-dihydrophosphindole was formed in high yield (93% in one experiment). A similar result was obtained for the dimer (**7**) of 1-phenylphosphole oxide. The structure of **6** and its *P*-sulfide was es-

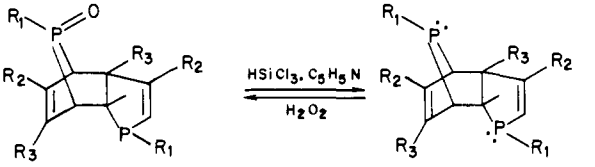


5, R = CH_3
7, R = C_6H_5

6
8

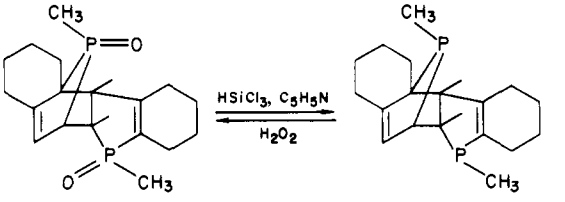
tablished by spectral examination; **8** has been described elsewhere.[20] Both reactions are preparatively useful for obtaining these new phosphines.

The course of these reductions, and of dimers **11**, **13**, **15**, and **17**, was completely different when pyridine was present; loss of the bridge was minor and the desired diphosphines were obtained in high yield. These compounds are formally the dimers of



5. R_1 = CH_3, R_2 = R_3 = H
7, R_1 = C_6H_5, R_2 = R_3 = H
11, R_1 = R_2 = CH_3, R_3 = H
13. R_1 = C_6H_5, R_2 = CH_3, R_3 = H
15. R_1 = R_2 = R_3 = CH_3

9 (84%)
10 (83%)
12 (82%)
14 (80%)
16 (96%)



17 **18**

phospholes, although no record exists of the dimerization of phospholes. In every case, the stereochemistry of the starting oxide was retained, since the diphosphines were converted to these oxides on hydrogen peroxide oxidation (a retention process[21]). Only minor amounts of inverted product were occasionally obtained.

All of these new diphosphines were stable at room temperature and the *P*-methyl compounds were vacuum distillable. The synthetic method is quite general and is the first to make the 7-phosphanorbornene system readily accessible.[22] The diphosphines were characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy (vide infra) and were analyzed as their disulfides or bis(methiodides). The bridging phosphorus gives a very far downfield signal (δ +97 to +120), which is a great aid in the product analysis.

Not all of the various oxides require the presence of pyridine with the trichlorosilane to prevent fragmentation; oxides **11** and **13** gave good yields of the diphosphines (**12**, 80%; **14**, 88%) on refluxing with trichlorosilane in benzene. On the other hand,

(14) Cremer, S. E.; Farr, F. R.; Kremer, P. W.; Hwang, H.-O.; Gray, G. A.; Newton, M. G. *J. Chem. Soc., Chem. Commun.* **1975**, 374.
(15) (a) Chang, L. L.; Denney, D. Z.; Denney, D. B.; Hsu, Y. F. *Phosphorus* **1974**, *4*, 265. (b) Scott, G.; Hammond, P. J.; Hall, C. D.; Bramblett, J. D. *J. Chem. Soc., Perkin Trans. 2* **1977**, 882.
(16) Hammond, P. J.; Lloyd, J. R.; Hall, C. D. *Phosphorus Sulfur* **1981**, *10*, 47.
(17) For a recent review, see: Mathey, F. *Top. Phosphorus Chem.* **1980**, *10*, 1.
(18) Quin, L. D.; Mesch, K. A.; Bodalski, R.; Pietrusiewicz, K. M. *Org. Magn. Res.* **1982**, *20*, 83.
(19) Kluger, R.; Kerst, F.; Lee, D. G.; Westheimer, F. H. *J. Am. Chem. Soc.* **1967**, *89*, 3919.
(20) Quin, L. D.; Rao, N. S. *J. Org. Chem.* **1983**, *48*, 3754.
(21) Horner, L. *Pure Appl. Chem.* **1964**, *9*, 225.
(22) The first 7-phosphanorbornene was formed in 3% yield from Diels–Alder reaction of pentaphenylphosphole with maleic anhydride (Braye, E. H.; Hubel, W. *Chem. Ind. (London)* **1959**, 1250). The Diels–Alder reaction was not shown to have further utility until 1981[4b] when it was applied directly to 1-phenyl-3,4-dimethylphosphole. The sulfide also gives a Diels–Alder adduct; this may be converted to P(III) form via a nickel complex.

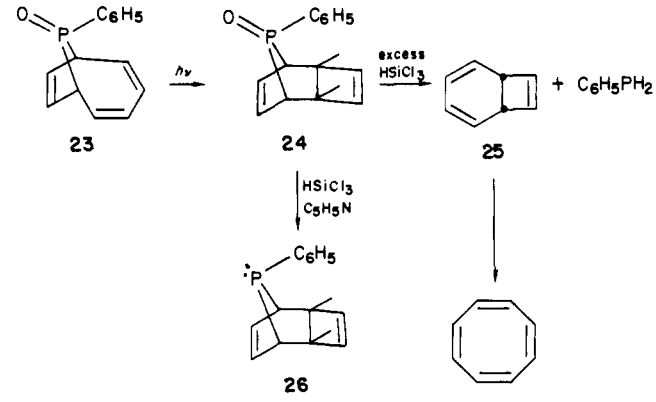
phenylsilane has uniformly given very poor yields of the *syn*-diphosphines; the major product is the quite unexpected diphosphine with anti structure from inversion at the bridging phosphorus. These phosphines, as well as **22** ($R_1 = C_6H_5$, $R_2 = H$), had been

19, $R_1 = CH_3$, $R_2 = H$ (65%), + **9** (25%)
20, $R_1 = R_2 = CH_3$ (67%), + **12** (27%)
21, $R_1 = C_6H_5$, $R_2 = CH_3$ (72%), + **14** (8%)

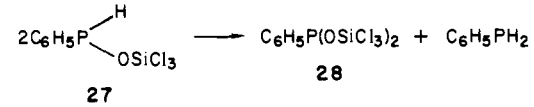
synthesized in earlier work[23] by isomerization of the syn isomers with methanol. Details of these experiments are reported herein. Some of the corresponding dihydrophosphindole (10–20%) is formed in each phenylsilane reduction, also implying that P(V) intermediates are involved.

Attempts to perform the deoxygenation of dioxide (**15**) with hexachlorodisilane gave a complex mixture. On the other hand, the trichlorosilane–triethylamine mixture reduced **11** with retention, albeit in low yield (34%).

The 7-phosphanorbornene system in the product (**24**) arising[24] from irradiation of the bicyclic phosphine oxide **23** lost the phosphorus bridge completely on trichlorosilane reduction, giving only phenylphosphine and cyclooctatetraene (from valence tautomerism[25] of **25**).



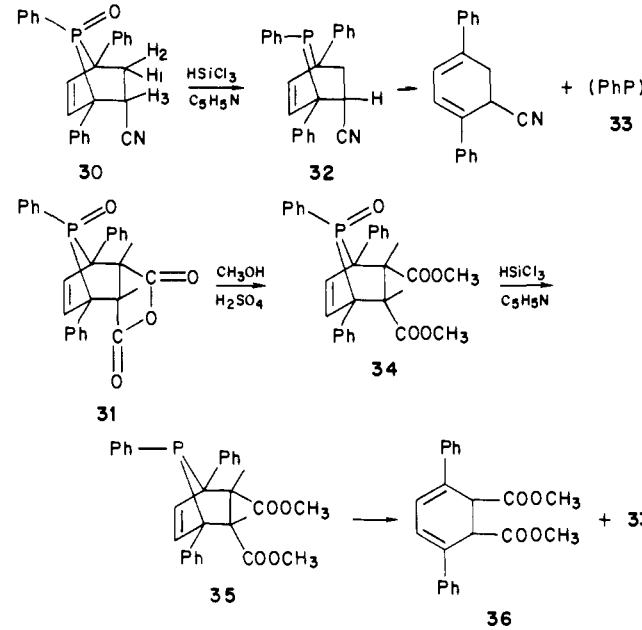
However, pyridine again prevented the retrocycloaddition and allowed the synthesis (80%) of the new *anti*-phosphine **26**. That retention occurred was proved by NMR spectral properties and by peroxide oxidation to re-form **24**. An earlier[23] interpretation of the ^{31}P spectrum (vide infra) had suggested the syn structure, which is now revised. An important mechanistic observation was made when the usual excess of trichlorosilane (without pyridine) was avoided and an equimolar amount with respect to oxide **24** was used; a new ^{31}P signal at δ +161.6 was observed. The similarity to the values of dialkyl phenylphosphonites (e.g., dimethyl,[26] δ +162) suggested that this product had structure **28**, resulting



along with phenylphosphine from disproportionation of the initial ejected fragment **27** from the retro-McCormack reaction. As reported previously,[23] a similar ejected fragment ($C_6H_5PHOCH_3$) from the addition product of methanol and **26** also underwent this disproportionation. The high reactivity of **28** has discouraged attempts at further characterization.

In work to be described elsewhere,[27] the syn isomer of phosphine oxide **24** was prepared and reduced to the authentic *syn*-phosphine (**29**) with the trichlorosilane–pyridine complex; its ^{31}P NMR spectrum is included in this paper (Table I).

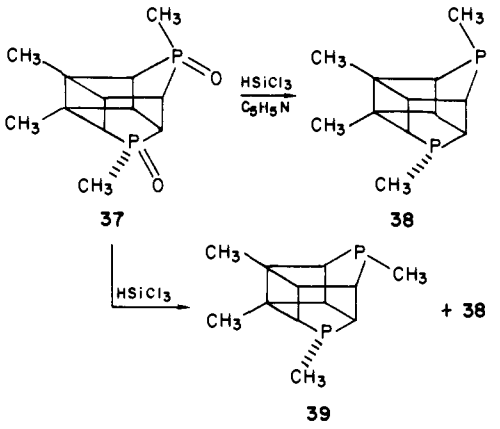
1,2,5-Triphenylphosphole oxide, one of the very few members of this family to resist dimerization, forms adducts with dienophiles that possess the 7-phosphanorbornene structure.[28] One adduct (**30**, whose stereochemistry is assigned from the ^1H and ^{13}C NMR



data given in the Experimental Section) and a derivative of another (**31**) were reduced with the trichlorosilane–pyridine complex. In each case, the reaction mixture gave a ^{31}P NMR spectrum containing the characteristic far-downfield signal of the expected phosphine (**32**, δ +129.7; **35**, δ +137.0). However, the major phosphorus product, even with pyridine present, proved to be the cyclotetraphosphine **33** ($n = 4$), $\delta(^{31}P)$ −47.9, an endproduct from the loss of the bridging phosphorus. Some $(C_6H_5P)_5$, $\delta(^{31}P)$ −4.2, was also formed. This decomposition during formation of the phosphines, which has prevented their isolation and full characterization, has not been encountered in any other case. After workup of the product, it was found that the phosphines were reasonably stable in refluxing benzene, implying that some characteristic of the original reaction medium was responsible for the considerable amount of fragmentation. In an experiment to be described in a later section, evidence was obtained that trichlorosilane itself can react with a particularly strained phosphine (**53**) to cause inversion, raising the possibility of its implication in the present case of fragmentation. Another peculiarity of this reduction is the extensive formation of the tetramer **33**; when *P*-phenylphosphole dimers decompose, it is the pentamer that results.

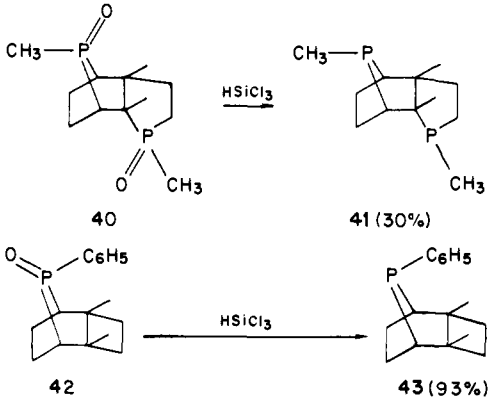
7-Phosphanorbornane Derivatives. The caged dioxide **37**, prepared by [2 + 2] intramolecular cycloaddition[29] of phosphole oxide dimer **11**, can be viewed as a highly strained 7-phosphanorbornane (both P groups are identical). Both the trichlorosilane–pyridine complex and phenylsilane reduced **37** smoothly to the diphosphine **38** as the only product ($\delta(^{31}P)$ −1.8). However, trichlorosilane alone gave erratic results, sometimes producing pure **38**, but on occasion forming also another diphosphine. This product is assigned structure **39**, wherein one phosphorus has undergone inversion. This was evident from the ^{31}P NMR spectrum which showed two signals (1:1, −15.1 and −17.2, $J \sim 0$) for the now nonequivalent nuclei, and from the fact that both **38** and **39** formed the same bis(methiodide). If inversion had

(23) Mesh, K. A.; Quin, L. D. *Tetrahedron Lett.* **1980**, 4791.
(24) Turnblom, E. W.; Katz, T. J. *J. Am. Chem. Soc.* **1973**, *95*, 4292.
(25) Huisgen, R.; Mietzsch, F.; Boche, G.; Seidl, H. *Spec. Publ. Chem. Soc.* **1964**, *19*, 3.
(26) Denney, D. B.; Denney, D. Z.; Hall, C. D.; Marsi, K. L. *J. Am. Chem. Soc.* **1972**, *94*, 245.
(27) Quin, L. D.; Rao, N. S., unpublished observations.
(28) Campbell, J. G. M.; Cookson, R. C.; Hocking, M. B.; Hughes, A. N. *J. Chem. Soc.* **1965**, 2184.
(29) Tomioka, H.; Hirano, Y.; Izawa, Y. *Tetrahedron Lett.* **1974**, 4477.

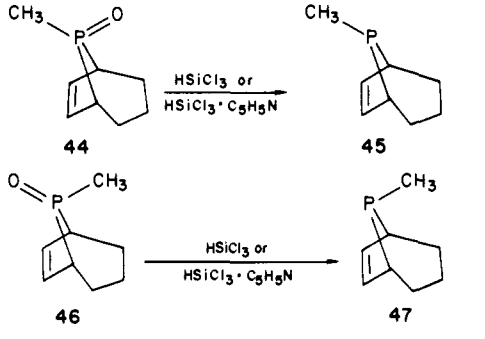


occurred at both phosphorus atoms, only one signal would have been observed for these chemically equivalent atoms. Compound **39** was also formed by causing **38** to undergo pyramidal inversion at 130° (in xylene); after 24 h, the ratio **38**:**39** was about 1:1. No evidence for the product of double inversion, either from silane reduction or thermal treatment, was obtained.

The saturated phosphine oxides **40** and **42** (previously reported from the hydrogenation of **18** and **24**,[24] respectively) gave only single products (**41** and **43**, respectively) with retained configuration when reduced with trichlorosilane alone. As usual, this was proved by oxidation of these new phosphines to the original oxides.



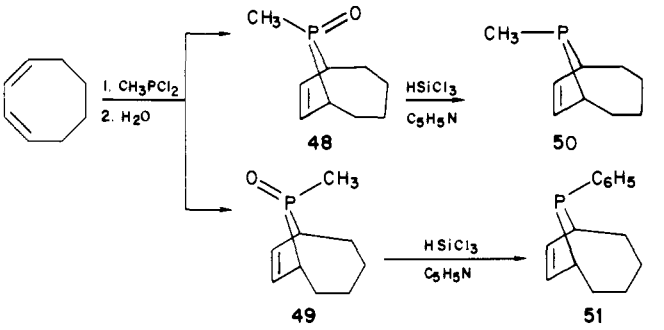
Other Phosphabicycloalkene Oxides. Although 1,3-cyclohexadiene and some derivatives failed in our hands to undergo the McCormack cycloaddition with P(III) halides, 1,3-cycloheptadiene reacted with CH_3PCl_2, as reported,[30] to give after hydrolysis the 8-phosphabicyclo[3.2.1]octene derivatives **44** (syn, 32%) and **46** (anti, 68%). We have reduced this mixture with



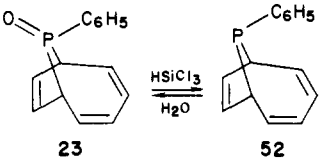
trichlorosilane alone or as its pyridine complex, obtaining in each case the same mixture of phosphines **45** and **47**, in the same ratio as the starting oxides. The isomeric phosphines gave the same methiodide, and peroxide oxidation produced the original oxide mixture. Oxide **46** was obtained in pure form by chromatography and gave only phosphine **47** with trichlorosilane.

On the other hand, a small amount (about 5%) of the product from the reduction of pure **46** with phenylsilane was the syn isomer **45**. Some loss of the phosphorus bridge by retro-cycloaddition occurred, since CH_3PH_2 was detected by ^{31}P NMR in the reaction mixture. Two other reducing systems that proceed through P(V) intermediates (hexachlorodisilane and trichlorosilane–triethylamine) gave only the product of retention with no indications of the retro-cycloaddition. Other strained ring systems, such as the phosphetane oxides,[31] usually react with these reagents with retention, although unstrained systems react with inversion.

1,3-Cyclooctadiene has now been found also to cycloadd, although slowly, with CH_3PCl_2; hydrolysis after 2 weeks of reaction at 120 °C gave only a yield of 4% of *syn*- (**48**, 82%) and *anti*- (**49**, 18%) 9-phosphabicyclo[4.2.1]non-2-ene oxides, detected by ^{13}C NMR spectroscopy. The mixture was reduced with $HSiCl_3$–pyridine to give the phosphines **50** and **51** in the same ratio as in the oxides.



The fully unsaturated 9-phosphabicyclo[4.2.1]nonatriene oxide **23** was reduced successfully with $HSiCl_3$ alone, giving the known[24] **52** as the only phosphine. No loss of the phosphorus bridge was noted and reoxidation gave the original oxide.



Monocyclic and Bridged Phosphetane Oxides. The contracted bond angle within the phosphetane system also causes this simple monocycle to give anomalous results on trichlorosilane reduction. A mixture of cis (42%) and trans (58%) isomers of 1-phenyl-2,2,3-trimethylphosphetane was formed on trichlorosilane reduction of a sample of the oxide that was 95% trans and 5% cis. However, when the reduction was effected with 3 molar equiv of the trichlorosilane–pyridine complex, complete retention was obtained, as observed also by Cremer and Chorvat[32] in a similar experiment. A mixture of isomers also has been reported[10] in a phenylsilane reduction of some 1-aryl-2,2,3,4,4-pentamethylphosphetane oxides. While retention is the common result of collapse of the TBP in other reductions and substitutions of phosphetanes,[31] inverted products can be formed by appropriate polytopal isomerizations of the TBP intermediate.

The highly strained bridged phosphetane oxide **2** is available from hydrolysis of the reaction product[14,33] of norbornadiene and methylphosphonous dichloride. Its structure has been confirmed by X-ray analysis[34] of a *p*-nitrobenzyl salt of the phosphine. We have found that even when pyridine is present in the trichlorosilane reducing medium extensive inversion occurs and a mixture of isomers is formed. If pyridine is omitted, inversion is complete.

(30) Kashman, Y.; Awerbouch, O. *Tetrahedron Lett.* **1970**, *26*, 4213.

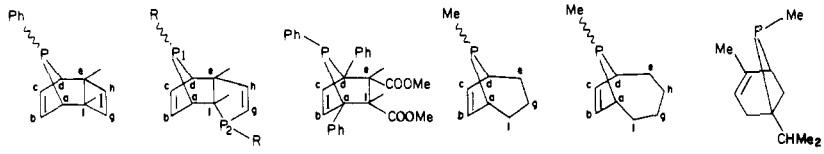
(31) Holmes, R. R. In "Pentacoordinated Phosphorus"; American Chemical Society: Washington, DC, 1980; ACS Monogr. No. 176, Vol. II, Chapter 2.

(32) Cremer, S. E.; Chorvat, R. J. *J. Org. Chem.* **1967**, *32*, 4066.

(33) Green, M. *J. Chem. Soc.* **1965**, 541.

(34) Mazhar-ul-Haque; Rashid, M.; Cremer, S. E. *J. Chem. Soc., Perkin Trans. 2* **1978**, 1115.

Table I. ^{31}P and ^{13}C NMR Data[a] for Bridged, Unsaturated Phosphines

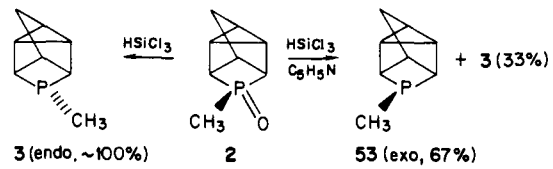


syn **29**, ant, **26** | **9**, **12**, **16**, **10**, **14**, **19**, **20**, **21**, **22** | **35** | **45**, **47** | **50**, **51** | **55**

	^{31}P			^{13}C							
compd	P_1	P_2	J_{PP}, Hz	a	b	c	d	e	f	g	h
26[b]	+98.8			41.4 (10.4)	*c*	*c*	41.4 (10.4)	48.5 (2.3)	48.5 (2.3)	138.2	138.2
29	+147.0										
9[b]	+96.5	−2.3	24.4	47.7 (9.8, 23.7)	133.2 (0, 9.8)[d]	132.7 (5.0, 0)	47.3 (9.2, 0)	57.3 (28.1, 4.8)	46.0 (29.3, 6.0)	133.8 (3.0, 15.8)	142.8 (10.8, 0)
12[e-g]	+100.8	−2.6	22.0	47.9 (9.8, 24.4)	126.4 (4.9, 8.8)[d]	142.1 (4.9, 0)	52.5 (9.8, 0)	60.1 (28.3, 4.9)	48.5 (24.4, 6.8)	129.2 (2.0, 15.6)	150.7 (9.8, 0)
16[b]	+98.8	−14.4	29.3	53.8 (9.2, 23.9)	133.7 (5.0, 5.0)	135.5 (4.2, 0)	60.4 (9.2, 1.2)	64.5 (19.5, 5.0)	54.2 (22.1, 6.0)	126.8 (2.4, 11.6)	155.3 (3.6, 0)
10[b]	+114.2	+15.7	24.4	47.9 (11.0, 26.9)	*c*	*c*	47.1 (11.0, 0)	57.2 (28.6, 4.2)	47.2 (25.1, 8.0)	*c*	145.0 (9.2, 0)
14[b]	+119.8	+15.0	24.0	47.7 (10.3, 26.7)	*c*	*c*	51.7 (9.8, 0)	59.8 (28.5, 4.2)	49.0 (24.3, 5.9)	*c*	153.8 (10.4, 1.8)
19	+30.2	−7.9	~0								
20[e,f]	+26.5	−9.6	4.9	44.5 (10.8, 24.4)	127.7 (19.5, 10.8)	143.9 (20.5, 0)	*c*	60.3 (3.9, 2.9)	*c*	128.4 (0, 14.7)	150.4 (0, 0)
21[b]	+48.5	+11.4	~0	45.6 (13.2, 27.5)	*c*	*c*	44.2 (11.5, 4.0)[h]	59.1 (3.3, 0)	48.6 (4.2, 7.7)[h]	*c*	*c*
22[b,i]	+44.9	+9.9	~0	44.9 (11.6, 27.5)	*c*	144.1 (20.3, 3.8)	50.1 (11.2, 0)	61.5 (3.2, 3.2)	48.8 (3.0, 11.1)	*c*	153.7 (0, 1.2)
35[e,j]	+137.0			64.6 (8.1)	*c*	*c*	64.6 (8.1)	56.6 (32.2)	56.6 (32.2)		
45[e]	+49.7			*c*	129.5 (6.6)	129.5 (6.6)	*c*	24.2 (16.5)	24.2 (16.5)	23.0 (0)	
47[e,k]	−18.2			33.1 (7.3)	133.0 (18.9)	133.0 (18.9)	33.1 (7.3)	17.1 (4.3)	17.1 (4.3)	18.8 (4.9)	
50[e]	−8.2			45.3 (11.0)	133.7 (5.5)	133.7 (5.5)	45.3 (11.0)	31.4 (17.6)	31.4 (17.6)	25.9 (8.8)	25.9 (8.8)
51[e]	−8.1			37.2 (6.6)	135.3 (16.5)	135.3 (16.5)	37.2 (6.6)	29.6 (5.5)	29.6 (5.5)	25.8 (0)	25.8 (0)
55[e,l]	+25.5			43.4 (3.3)	118.1 (12.1)	144.4 (5.5)	40.3 (4.4)	30.3 (0)	31.5 (0)		

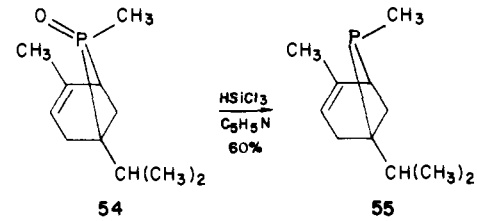
[a] Taken on $CDCl_3$ solutions unless otherwise noted. P values are given in δ. Values in parentheses are (J_{C-P_1}, J_{C-P_2}) in Hz. CH_3 signals: **9**, P_1 6.8 (26.1, 1.2) and P_2 15.3 (0, 20.1); **12**, P_1 7.0 (29.3, s; J_{C-P_2} = 1.2 Hz observed at 15 MHz) and P_2 16.1 (0, 22.5); **16**, P_1 6.4 (26.3, 3.0) P_2 CH_3 overlapped with C–CH_3 at 15.6–17.6; **20**, P_1 11.7 (34.2, 2.0) and P_2 16.0 (0, 22.5); **47**, 8.8 (31.1); **50**, 8.9 (17.6); **51**, 6.3 (23.1); **55**, 7.4 (35.2). [b] ^{13}C NMR taken with JEOL FX-60 at 15.5 MHz. [c] Not clearly distinguished. [d] Coupling constants could be reversed. [e] Taken with JEOL FX-90 Q at 22.5 MHz. [f] C_6D_6 solution. Spectrum published in: "Selected ^{13}C Nuclear Magnetic Resonance Spectral Data"; Supplementary Volume No. G-12; Thermodynamics Research Center, Texas A&M University, College Station, TX, 1982. Assignments to some carbons are revised with the recognition that e is specially deshielded as in dicyclopentadiene (δ 54.8): Nakagawa, K.; Iware, S.; Ishi, Y.; Ogawa, M. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2391. [g] C–CH_3 at 15.6–17.6. [h] Assignment uncertain. [i] C–CH_3 at 19.2–19.4. [j] $COOCH_3$ at 170.3 (s) and 51.5 (s), respectively. [k] ^{13}C NMR previously reported: Rudi, A.; Kashman, Y. *Org. Magn. Reson.* **1977**, *10*, 245. [l] ^{13}C previously reported.[36b]

This inversion has been noted by others[14] and attributed to the presence of HCl in the medium; freshly distilled trichlorosilane was used in our experiment to eliminate this possibility. That some inversion occurs even when pyridine is present also speaks against a role for HCl in the inversion.



We have noted yet another peculiarity with this especially strained system; heating the **53**–**3** mixture, after isolation, with trichlorosilane caused complete isomerization of **53** to **3**. A possible mechanism might involve a P(V) adduct with the phosphine and trichlorosilane, as has been encountered[13,35] when silicon tetrachloride causes inversion of a phosphetane. This prompted a test of the behavior of a phosphine with the phosphole dimer system (**12**) toward trichlorosilane, but no inversion occurred, and for the present the case of phosphine **53** seems to be unique. The failure of pyridine to give effective control in the trichlorosilane reduction of **2** also is unique among the strained compounds so far studied.

Another bridged phosphetane oxide **54** results from hydrolysis of the reaction product of α-pinene with methylphosphonous dichloride in the presence of $AlCl_3$.[36] For this compound, we had earlier[36b] found that the trichlorosilane–pyridine reduction was stereospecific, providing the phosphine (**55**) with retained configuration.



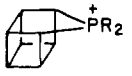
54 **55**

(35) DeBruin, K. E.; Zon, G.; Naumann, K.; Mislow, K. *J. Am. Chem. Soc.* **1969**, *91*, 7027.

(36) (a) Vilkas, E.; Vilkas, M.; Joniaux, D.; Pascard-Billy, C. *J. Chem. Soc., Chem. Commun.* **1978**, 125. (b) Quin, L. D.; Kisalus, J. C.; Mesch, K. A. *J. Org. Chem.* **1983**, *48*, 4466.

We have now performed the reduction in the absence of pyridine, but obtained only a complex mixture that contained none of **55**. The phenylsilane reduction was also attempted, but similar results were obtained. The anti isomer has not yet been successfully produced.

Summary of Observations. It is apparent from the many examples in this work that applying generalities on silicon hydride reductions ($HSiCl_3$ or $C_6H_5SiH_3$) to highly strained phosphine oxides can lead to erroneous predictions of the stereochemical outcome. That the intervention of P(V) intermediates accounts for the isomerization is supported by the observation of another reaction, retro-cycloaddition in the 7-phosphanorbornene series, that *requires* such intermediates. That the P(V) state is especially readily formed from strained phosphorus compounds is not a new concept; a pertinent example[24] is the tendency of the highly strained cyclic phosphonium ion (**56**) to add an alkyl anion and give a stable pentaalkylphosphorane, rather than lose an α-proton in the customary way.

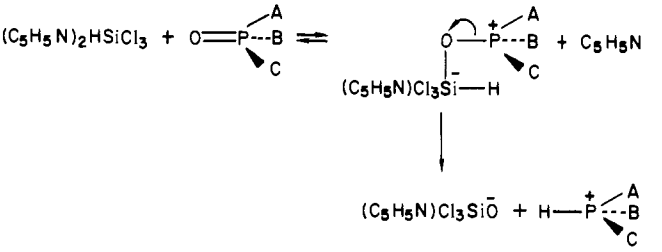


56

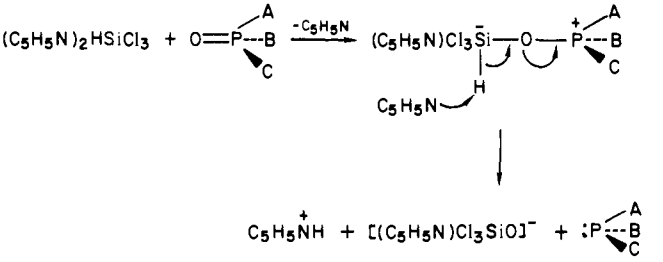
The TBP structure offers two bond angles to the substituents: 120° for those in the equatorial plane, 90° to an apical–equatorial disposition. Adopting the latter angle can relieve the strain imposed by ring structure on P(IV) or P(III) groups, which in acyclic compounds are known to have bond angles of 100° or more.[37] The bond angles in some of the strained frameworks of the present study are reduced by 20° or more from this value (e.g., 83° in **11**;[38] 76.9° in **54**;[38] 74.8° in the *p*-nitrobenzyl bromide salt from **3**[34]). At the same time, it cannot be concluded that all bridged or angle-contracted species will react through P(V) intermediates, or that even when P(V) is achieved the consequences of polytopal isomerization, or of retro-cycloaddition where possible, will occur. Nevertheless, some trends may be detected from our survey that may prove useful in the study of other systems. (1) When P spans the 1,4-positions of a cyclohexene, as in the 7-phosphanorbornenes, P(V) intermediates can usually be expected; isomerization and/or retrocycloaddition are likely. It is not surprising that earlier workers[39,40] experienced loss of the P bridge on attempted reduction of a 7-phosphanorbornadiene oxide with $HSiCl_3$ or $C_6H_5SiH_3$; it is possible that the resulting phosphine would be stable enough for detection if the P(V) intermediate and consequent retro-cycloaddition were avoided. (2) Expanding the methylene chain in the cycloalkene appears to relax the angle contraction, and when P(V) intermediates are formed, they do not isomerize or undergo significant retro-cyclization before decomposition to phosphines. Thus, 1,4-bridging of cycloheptene and cyclooctene as in **44** and **48** gives phosphine oxides that respond quite normally to trichlorosilane alone. (3) Saturated bridged structures can also undergo the reductions with isomerization. Although the two phosphanorbornanes **40** and **42** only give the products of retention with $HSiCl_3$, the strain of additional bridging as found in **37** caused (on occasion) some inversion to occur, and this becomes the only result when the strain reaches that imposed on **2**. (4) Saturated monocyclic compounds respond normally (giving retention) to the silanes until the severe angle contraction (to around 80°[41]) of the phosphetane ring is reached. Variable results, apparently dependent on other structural features, can then be obtained. Much inversion accompanied the $HSiCl_3$ reduction of 1-phenyl-2,3,3-trimethylphosphetane oxide and the $C_6H_5SiH_3$ reduction[10] of several 1-aryl phosphine oxides based on 2,2,3,4,4-pentamethylphosphetane. On the other hand, reports are more common in the literature for complete retention with these reagents when applied to phosphetane oxides. For example, retention occurred in the $HSiCl_3$ reduction in $CHCl_3$ at 0 °C of *cis*- or *trans*-2,2,3,4,4-pentamethyl-1-phenylphosphetane 1-oxide,[42] in the $HSiCl_3$ reduction in benzene at reflux of 4-bromo-2,2,3-trimethyl-1-phenylphosphetane 1-oxide,[43] and of 1-phenyl-2,2-dimethylphosphetane 1-oxide.[44]

In TBP intermediates from highly strained ring systems it is thought the ring retains an apical–equatorial disposition. Requirements of apical entry and departure in TBP structures suggest that for retention, one pseudorotation is required, but for inversion a second is required. These points are discussed in detail elsewhere;[11,31] no special extension is required to accommodate results of the present study.

The discovery that pyridine prevents the complications of P(V) intermediates in the $HSiCl_3$ reduction of strained heterocyclic phosphine oxides has some very practical consequences. It has allowed the facile synthesis of the first examples of phosphines in the 7-phosphanorbornene system. It has prevented the formation of isomeric mixtures in all but one (on the unusually strained **2**) of the other reductions performed. The trichlorosilane–pyridine complex therefore is the reagent of choice in reduction of strained oxides and is more reliable than the otherwise excellent phenylsilane. Just how the presence of complexed pyridine brings about the considerable modification of the character of trichlorosilane is not clear, nor for that matter is the structure of the complex. It is known[45,46] to have the composition $(C_5H_5N)_2HSiCl_3$, with retention of the Si–H bond, but other features are less certain. Trichlorosilane itself appears to function as a hydride donor to phosphorus (Scheme I), and in so doing has the capability in some cases of creating P(V) intermediates. This would suggest that the pyridine complex does not act as a hydride donor, or if it does it is incapable of creating a P(V) intermediate. The original mechanism put forward by Horner and Balzer[8] takes the latter view, without assigning a direct role to the pyridine.



In the modification outlined below, pyridine serves to remove hydrogen from the complex with the phosphine oxide, preventing hydride donation to phosphorus and thus the creation of a P(V) intermediate.



^{13}C NMR Spectra. Experimental data for those phosphines having the phosphabicycloalkene structural feature are collected in Table I to facilitate the detection of correlations. Data for other

(37) Daly, J. J. In "Perspectives in Structural Chemistry"; Dunitz, J. D.; Ibers, J. A.; Eds.; Wiley: New York, 1970; Vol. III, pp 172–214.
(38) McPhail, A. T., unpublished results.
(39) Schmidt, U.; Boie, I.; Osterroht, C.; Schröer, R.; Grützmacher, H. *Chem. Ber.* **1968**, *101*, 1318.
(40) Stille, J. K.; Eichelberger, J. L.; Higgins, J.; Freeburger, M. E. *J. Am. Chem. Soc.* **1972**, *94*, 4761.
(41) Fitzgerald, A.; Campbell, J. A.; Smith, G. D.; Caughlan, C. N.; Cremer, S. E. *J. Org. Chem.* **1978**, 3513.
(42) Corfield, J. R.; Harger, M. J. P.; Shutt, J. R.; Trippett, S. *J. Chem. Soc. C* **1970**, 1855.
(43) Mazhar-ul-Haque; Horne, W.; Cremer, S. E.; Kremer, P. W.; Kafarski, P. K. *J. Chem. Soc., Perkin Trans. 2* **1981**, 1138.
(44) Gray, G. A.; Cremer, S. E.; Marsi, K. L. *J. Am. Chem. Soc.* **1976**, *98*, 2109.
(45) Campbell-Ferguson, H. J.; Ebsworth, E. A. V. *J. Chem. Soc. A* **1967**, 705.
(46) Wannagat, U.; Hensen, K.; Petesch, P. *Monatsh.* **1967**, *98*, 1407.

phosphines are provided in the Experimental Section. Emphasis in the discussion of the data will be placed on special effects arising at carbons attached to or influenced by the bridging phosphorus and on a comparison of spectral features in syn,anti pairs.

(a) Phosphorus-Bound Carbons. The contraction of the internal C–P–C angle is accompanied by diversion of s-character from the bonds to the ring carbons into the bond to the exocyclic carbon. This is seen from the directly connected P–C coupling constants for the compounds of Table I, as well as in the saturated diphosphine **41**, which diminish in the ring carbons but become very large in the exocyclic carbon. The effect is present in phosphetanes as well,[44] and is the subject of a recent study in other systems.[47] The bridgehead carbons (a and d) in all of the structures in Table I (except **55**) have $^1J_{PC}$ in the range 7–11 Hz. An exocyclic methyl can have values as great as 35 Hz (**55**) which is one of the largest $^1J_{PC}$ for a tertiary phosphine ever recorded. A second consequence of the hybridization change occurs on the chemical shift for the exocyclic *P*-methyl; the values in all of the bridged structures are at δ 6–10, the upfield end of the region usually occupied by *P*-methylphosphines. This can be viewed as resulting from increased diamagnetic shielding by the increased s-character and to decreased paramagnetic shielding by the decreased p-character. However, steric compression effects from γ-related carbons also influence these chemical shifts and contribute to the shielding.

A pair of *syn-/anti*-7-phosphanorbornenes has an important ^{13}C difference in the values for the exocyclic P substituent. Thus, the *syn*-methyl of **11** has δ 7.0, ^1J = 29.3 Hz, while the methyl of the anti isomer (**20**) has δ 11.7, ^1J = 34.2 Hz. In the [4.2.1] series, the *anti*- (**51**) again has the larger ^1J (23.1 Hz, relative to 17.6 for *syn*-, **50**), but the order of the chemical shifts is reversed, probably due to difference in steric compression effects from the saturated carbons. Similar coupling and shift variations for an exocyclic carbon are found among monocyclic phosphorinanes,[48] where the more crowded isomer with axial *P*-methyl has a more upfield shift and smaller $^1J_{PC}$ relative to that with equatorial *P*-methyl. This difference in the syn,anti isomers may imply that a difference exists in the hybridization at phosphorus in the isomers. Alternatively, the difference in steric crowding in the isomers may influence $^1J_{CP}$; it is known that $^1J_{CH}$ for the two protons at the 7-position of norbornenes differs,[5] an effect attributed to steric crowding. However, the more crowded anti proton has the smaller $^1J_{CH}$, while the more crowded *anti*-PCH_3 group has the larger $^1J_{CP}$. The complexity of the coupling phenomenon does not allow an immediate explanation for the C–P effect.

Pronounced changes in $^1J_{PC}$ occur on lengthening the saturated chain (*n*) in the bicyclo[*n*.2.1]alkene series. In the anti series, $^1J_{PC}$ to the exocyclic methyl diminishes regularly as *n* is increased (**20**, *n* = 2, *J* = 34.2 Hz; **47**, *n* = 3, *J* = 31.1 Hz; **51**, *n* = 4, *J* = 23.1 Hz). The effect is present also in the syn series (**5**, *n* = 2, *J* = 26.1 Hz; **50**, *n* = 4, *J* = 17.6 Hz). The last value is similar to that of a monocyclic 3-phospholene (1,3-dimethyl,[49] $^1J_{PCH_3}$ = 15.6 Hz) and suggests no special strain to be present in this [4.2.1]system. Similar relaxation of strain occurs in the related carbocyclic compounds of the bicyclo[*n*.2.1] series[50] and is manifested in chemical reactivities.

A significant difference occurs in $^1J_{PC}$ values for the ring carbons in the [*n*.2.1] series. In the syn members of the series, the value increases, as expected, with ring size (**5**, *J* = 9.2, 9.8 Hz; **50**, *J* = 11.0 Hz) while in the anti series, the value decreases (**20**, 10.8 Hz; **47**, 7.3 Hz; **51**, 6.6 Hz). This is one of the only ways in which syn,anti isomers differ in their ^{13}C NMR trends; other coupling and shift differences are readily explained on well-established grounds. In a pair of syn,anti isomers, however, there is no more than 1–2 Hz difference in the $^1J_{PC}$ values. A more striking effect at these bridgehead carbons results from the proximity (two bonds) of one of them (carbon a in Table I) to the 2-phospholene phosphorus (P_2). The two-bond coupling is consistently very large (24–27 Hz) in both syn and anti isomers; its size results from the geometric relation of carbon a to the lone pair on P_2, a well-documented effect among phosphines.[2] Bridgehead carbon d is three-bond related to P_2, but here dihedral angle effects in the P_2–C–C–C_a unit are in control, and the approximate angle of 120° is such as to suggest a small coupling.[51] In fact, only 0–2 Hz is observed.

(b) Two- and Three-Bond Effects of Bridging Phosphorus. For carbons separated from phosphorus, the rigid 7-phosphanorbornene system allows pronounced differences to develop in syn and anti isomers. Numerous examples of the stereospecificity in $^2J_{PC}$ can be seen. Thus, in all syn compounds the C=C unit (carbon b, c) has a small $^2J_{PC}$ (3–5 Hz), while the saturated bridge carbons (e, f) have $^2J_{PC}$ exceeding 20 Hz. The reverse occurs in the anti isomers; $^2J_{PC}$ for the C=C unit is about 20 Hz while it is about 3 Hz for the saturated carbons. These effects make it a simple matter to assign syn,anti structure in bridged systems; they are also present in the more flexible bicyclo[3.2.1] and -[4.2.1] systems. Even when only a single isomer is available, as in **26** and **35**, the stereostructure can be assigned with confidence from these *J* values. Thus **26** is anti from the coupling to carbons e and f of only 2.3 Hz, whereas **35** is syn from the value of 32.2 Hz. The *J* stereospecificity effect is obvious in other systems as well. For example, in the caged structure **38**, the easily recognized quaternary carbon at 53.1 shows no coupling to ^{31}P, consistent with its remoteness from the lone pair.

Steric compression effects from the P-substituent also cause useful differences among syn,anti isomers in the phosphole dimer series; the unsaturated carbons b and c of the syn isomer **11** (Table I) are found 2–3 ppm upfield of the anti isomer (**20**). The reverse is observed for carbons e and f. The effect at e and f is especially strong (7.1 ppm) in the [3.2.1] series (**45**, **47**). This value is similar to that found[48] at C-3,5 in phosphorinanes with axial or equatorial P-substituents, an effect accounted for by viewing the [3.2.1] system as a phosphorinane with a 2,5-bridge. Similar observations have been made on ketones of this series.[52]

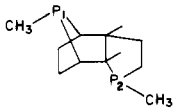
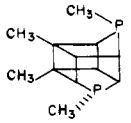
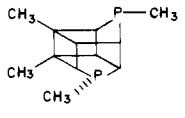
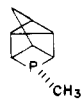
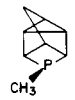
(c) Influence of Lone-Pair Orientation on $^3J_{PC}$ and $^4J_{PC}$. In freely rotating tertiary phosphines, $^3J_{PC}$ is controlled by a Karplus-like dependence on the dihedral angle.[51] In restricted systems, lone pair orientation effects operate also on $^3J_{PC}$, as has been recently demonstrated among phosphorinanes.[52] The systems of the present study provide further examples of the effect. Thus, $^3J_{PC}$ for carbon h in a *syn*-phosphole dimer (**12**) is about 10 Hz, while the *anti*- (**20**) shows no coupling, even though the dihedral angle would be approximately the same in the isomers.

The rigid 7-phosphanorbornene system also provides examples where a lone pair orientation effect on $^4J_{PC}$ seems to be present. Carbon g shows small coupling (2.0 Hz) in the syn isomer (**11**), but no apparent coupling in the anti isomer (**20**). The unusual effect of transmission through the four-bond unit CH_3–P–C–C–P can be seen in **5**, where the CH_3 on the bridging P is a quartet with large $^1J_{PC}$ (29.3 Hz) and small $^4J_{PC}$ (1.2 Hz), while the 2-phospholene P is merely a doublet ($^1J_{PC}$ = 20.1 Hz).

(d) Second-Order ^{13}C Spectra. The spectrum of **41** is of special interest because the proximity of the ^{31}P shifts ($\Delta\delta$ 3.7) gives a second-order (AB) ^{31}P spectrum, and second-order effects are imparted to some ^{13}C signals (X in an ABX pattern). This effect has also been reported for the dioxide.[18] Coupling constants cannot be taken directly from such spectra unless run at high field to eliminate the second-order effect. Phosphine **38**, as true also for the dioxide,[18] gives second-order spectra due to magnetic nonequivalence of the ^{31}P nuclei; ^{13}C can therefore have the characteristics of X in an AA'X pattern, also precluding direct observation of the coupling constants. The spectra of these phosphines have not been fully interpreted. However, the expected effects

(47) Zschunke, A.; Meyer, H. *Phosphorus Sulfur* **1980**, *9*, 117.
(48) For example, 9.2 ppm in the isomers of 1-methyl-4-*tert*-butyl-4-phosphorinanol. Featherman, S. I.; Quin, L. D. *Tetrahedron Lett.* **1973**, 1955.
(49) "Selected ^{13}C Nuclear Magnetic Resonance Spectral Data"; Spectrum No. 805, Supplementary Volume No. G-12; Thermodynamics Research Center, Texas A&M University: College Station, TX, 1982.
(50) Hess, B. A. *J. Am. Chem. Soc.* **1969**, *91*, 5657 and references cited therein.
(51) Quin, L. D.; Gallagher, M. J.; Cunkle, G. T.; Chesnut, D. B. *J. Am. Chem. Soc.* **1980**, *102*, 3136.
(52) Pietrusiewicz, K. M. *Org. Magn. Reson.* **1983**, *21*, 345.

Table II. ^{31}P NMR of Saturated Phosphines

compd	structure	$\delta(^{31}P_1)$	$\delta(^{31}P_2)$	$^3J_{PP}$, Hz
41		−18.0	−21.7	22.0
38		−1.8		
39		−15.1	−17.2	~0
43		+22.0		
3		+39.5		
53		+47.4		

at carbons bonded to the bridging phosphorus in **41** are evident; the P–CH_3 group is shifted well upfield (δ 4.8) and has a large $^1J_{PC}$ value of about 28 Hz. These values are very similar to those of the unsaturated counterpart **11**. In phosphine **38** the methyl signal is well upfield (δ 4.8).

^{31}P NMR Spectra. The data for the bridged saturated phosphines of the present study are collected in Table II; considerable variation in δ ^{31}P is present (−18.0 to +47.4), but values are within the range found for acyclic phosphines (trimethyl, δ −62; tri-*tert*-butyl, δ +62). The contracted C–P–C bond angle in these structures (and by inference, in the unsaturated structures as well) therefore does not seem to cause any special effect. In the 7-phosphanorbornane **41**, for example, the bridging P and the phospholane P differ by only 3.7 ppm, an effect which makes the spectrum have second-order (AB) characteristics. A further reduction in bond angle probably is present in the bridged phosphetanes **3** and **49** but need not be associated with their somewhat more downfield position since other structural changes also are present. Isomers differing in configuration at P are possible for all of the compounds, but data in Table II show that their ^{31}P values will not be greatly different (**30**, $\Delta\delta$ 2.1; **3**–**53**, $\Delta\delta$ 7.9). This will be seen to be a profound difference relative to some of the unsaturated compounds.

The most unusual effect noted in this study (and later by others[4b]) is that replacement of a CH_2CH_2– unit in a 7-phosphanorbornane with a –CH=CH– unit causes very strong downfield shifting of the ^{31}P resonance. In the *anti*-phosphole dimer series, values in the δ range +30 to +50 are observed, representing a 50–70-ppm displacement from the saturated model **41**. The effect is far more pronounced in the syn than in the anti isomers, making the *syn*-7-phosphanorbornene series routinely have the most downfield values ever recorded for tertiary phosphines. The values (Table I) are grouped in the δ range +95 to +120 (ethiodide formation[4a] at P_2 of **10** results in δ +147.1 for P_1). When these observations were first made, the only similar effect in the literature[53] was the modest 10-ppm downfield shift of the ^{13}C signal at C-7 of norbornene (δ 48.8) from that of norbornane (δ 38.7). Very recent reports make it clear, however, that heteroatoms at the 7-position in general will experience very large deshielding, and the effect is no longer thought to be unique to phosphorus. Examples have been described where ^{29}Si[54] and ^{17}O[55] exhibit the effect, and in our laboratory we have found that ^{15}N in 7-azanorbornenes has shifts that are the lowest ever recorded for tertiary amines.[56] It has been stated[54,57] that the concept of ground-state polarization arising from σ–π conjugation provides an explanation for the effect since this type of hyperconjugation is of general importance in strained systems. This conjugative effect creates positive character at the 7-position, causing the deshielding. Other orbital interactions may be involved, but for the present we will use the σ–π conjugation proposal to account for the ^{31}P results. The downfield shifting is clearly not a result of the bond-angle contraction; in the saturated diphosphine **41**, the bond angle remains small but the ^{31}P chemical shift has moved nearly 100 ppm upfield from the unsaturated structure. The strong deshielding effect is also present in P(IV) derivatives of the phosphole dimers[18] and absent in their saturated derivatives. The phosphines of the 7-phosphanorbornene series still remain as novelties, however, for in no other case has such a large chemical shift difference developed between syn and anti isomers. A second strong influence is present, which is either adding to the σ–π deshielding in the syn form or is providing shielding to moderate this effect in the anti isomer. It has already been pointed out that there are significant differences in hybridization at P in the isomers, as revealed by the larger $^1J_{PC}$ value for exocyclic carbon in an anti isomer than in syn. Tertiary phosphine shifts are very sensitive to geometry and the steric environment at P, and firm structural parameters from an X-ray analysis of a syn,anti pair would be helpful in further probing of this shift effect. It is not possible to say if a hybridization difference is the cause of the effect or is associated with nonbonded interactions that separately influence chemical shifts. If the view is taken that a special shielding effect is present in the anti isomer, an obvious interaction to consider is repulsion between the lone pair and the π electrons. Such interactions have considerable importance in 7-azanorbornene properties.[58] The diversion of electron density onto phosphorus could increase the diamagnetic shielding, as well as cause a change in hybridization. The p-orbitals of sp^2 carbons are known not to be as sensitive to distortion by such interactions[57] which would explain why there are no accompanying effects on ^{13}C shifts in syn,anti pairs. It is also possible that some interaction of the π-electrons with phosphorus d-orbitals is involved, although tertiary phosphines generally make little use of their d-orbitals. Further considerations of these proposed interactions from a theoretical viewpoint seem called for.

Another structural change bearing on this matter is that of the lengthening of the saturated segment in a phosphabicycloalkene. When the segment increases from 2 to 3 carbons, as in the bicyclo[3.2.1]octene series **45** (syn) and **47** (anti), the syn,anti difference remains the same at about 70 ppm as in the comparable phosphole dimers (**5** and **19**), but there is a marked upfield shifting of both signals (about 50 ppm). These observations strengthen the case for the presence of two chemical shift effects; the deshielding seen in the norbornene framework is diminished as the CH_2 segment is increased and strain is partially relieved, but the strong syn,anti effect remains. When the saturated segment is increased to four carbons, as in **50** and **51**, *both* effects vanish; the chemical shifts for syn,anti isomers are virtually identical, and in a perfectly normal range (δ −8). The same ^{31}P chemical shift trend is seen in the oxides of the phosphabicyclo[*n*.2.1]alkene series (**5**, n = 2, δ +86.8; **44**, n = 3, δ +69.4; **48**, n = 4, δ +64.3), as

(53) Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972; Chapter 3.

(54) Sakurai, H.; Nakadaira, Y.; Koyama, T.; Sakaba, H. *Chem. Lett.* **1983**, 213.

(55) Nguyen, T. T.; Delseth, C.; Kintzinger, J.-P.; Carrupt, P.-A.; Vogel, P. *Tetrahedron* **1980**, *36*, 2793.

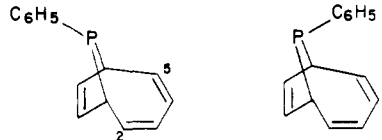
(56) Quin, L. D.; Miller, J. A.; Caster, K. C., unpublished results.

(57) Christl, M.; Herbert, R. *Org. Magn. Reson.* **1979**, *12*, 150.

(58) Yoshikawa, K.; Bekki, K.; Karatsu, M.; Toyoda, K.; Kamio, T.; Morishima, I. *J. Am. Chem. Soc.* **1976**, *98*, 3272. The repulsive interaction causes the syn isomer to be the more stable in this system. No difference in the ^{13}C signals for the sp^2 carbons, other than the normal γ-effect of the *syn*-methyl, was observed.

well as in the corresponding hydrocarbons (norbornene, δ 48.5;[59] bicyclo[3.2.1]octene, δ 45.1;[59] bicyclo[4.2.1]nonene, δ 31.5 or 33.6)[60]).

Turnblom and Katz had earlier[24] noted a great difference in the ^{31}P shifts of the fully unsaturated derivatives **57** and **58** of the 9-phospha[4.2.1]nonane system.



57 (δ -14) **58** (δ -79)

Installation of double bonds in the four-carbon segment is seen to restore the syn,anti difference that we have noted to be absent in the saturated compounds **50** and **51**. The diminished flexibility in the unsaturated system may be responsible for the restoration of the proposed lone pair repulsion and shielding in the anti isomer.

It has only recently[61] been reported that ^{31}P–^{31}P coupling is influenced by the dihedral angle relation; the rigid framework of dimers of phosphole oxides and sulfides has provided valuable new examples for observing the effect. This framework has now allowed us to make another observation on ^{31}P–^{31}P coupling: in phosphines (and probably other P(III) forms), the lone pair orientation is of great importance and, just as is true for ^{13}C–^{31}P coupling, can reduce ^{31}P–^{31}P coupling to very small values when the lone pair is remote. It is for this reason that all of the dimers in Table I with syn geometry have large $^3J_{PC}$ (24–29 Hz) values while the anti isomers have small values (0–5 Hz). In both situations the dihedral angle relation of the nuclei is essentially the same. In the syn isomer, the lone pair on the bridging phosphorus is directed toward the 2-phospholene phosphorus (the lone pair on the latter is directed away from the bridging phosphorus). Coupling is therefore permitted. In the anti isomer, neither lone pair is directed toward a coupled phosphorus, and coupling is quite small. The effect is not unique to the phosphole dimer framework; it is seen also in the failure to observe any coupling between the phosphorus nuclei of the saturated diphosphine **39** with the rigid cage structure. The disposition of the lone pairs resembles that in the *anti*-phosphole dimers.

Experimental Section

General. Proton NMR spectra were obtained on a JEOL MH-100 or an IBM NR-80 spectrometer at 100 and 80 MHz, respectively, using tetramethylsilane (Me_4Si) as an internal standard unless otherwise noted. Phosphorus-31 spectra (FT) were obtained on a JEOL FX-90Q or a Bruker HFX-10 spectrometer at 36.2 and 36.4 MHz, respectively, using 85% phosphoric acid (H_3PO_4) as an external standard with an internal deuterium lock. Negative shifts are upfield and positive shifts downfield of the reference. Carbon-13 spectra (FT) were obtained on a JEOL FX-90 Q or a JEOL FX-60 spectrometer at 22.5 and 15.0 MHz, respectively, using Me_4Si as internal standard unless otherwise noted. Broad-band proton noise decoupling was employed on all carbon-13 and phosphorus-31 NMR spectra. All coupling constants (*J* values) are given in hertz. Mass spectra (70 eV) were obtained on a Hewlett-Packard 5992A GC-MS or on the AEI MS 903 spectrometer at the Research Triangle Mass Spectrometry Center. Melting points were taken on a Mel-Temp apparatus and are corrected; boiling points are uncorrected. Combustion analyses were performed by MHW Laboratories, Phoenix, AZ, or Galbraith Laboratories, Knoxville, TN. Manipulations of phosphines were performed under nitrogen or argon.

General Procedure for $HSiCl_3$–C_5H_5N Reduction and Characterization of Phosphole Oxide Dimers. To a mixture of 5 molar equiv of trichlorosilane, 15 molar equiv of pyridine and 50 mL of benzene was added about 1–3 g of the phosphole oxide dimer. The mixture was refluxed for 1–2 h and then cooled in an ice–water bath while being hydrolyzed with excess 30% NaOH solution. The organic phase was separated, extracted with benzene, dried over $MgSO_4$, and concentrated under vacuum to give the corresponding phosphole dimer in high yield and purity. Methiodides, which occasionally were unstable, were prepared in pentane with methyl iodide and recrystallized from methanol. Sulfides were prepared using 2 molar equiv of sulfur. The product that precipitated after overnight standing at room temperature was collected and recrystallized from methanol. The compounds prepared were as follows.

1,*syn*-8-Dimethyl-3a,4,7,7a-tetrahydro-4,7-phosphinidene-1(*H*)-phosphindole (9). From 1.0 g (4.5 mmol) of **5**[18] was obtained 0.8 g (84%) of **9**, bp 75–78 °C (0.03 mm, Kugelrohr), as a clear oil: ^1H NMR ($CDCl_3$) δ 1.16 (d, $^2J_{PH}$ = 2 Hz, both P-CH_3 6 H), 2.97 (m, —C*H*—, 3 H), 4.41 (m, —C*H*—, H-3a), 5.80–6.60 (m, —C*H*=, 4 H); ^{13}C and ^{31}P NMR data, Table I. Bis(methiodide): mp 197–199 °C dec, lit.[62] 190–194 °C; ^{31}P NMR (D_2O) δ +98.3 and +58.8 (both d, $^3J_{PP}$ = 35.5). Anal. Calcd for $C_{12}H_{20}I_2P_2$: C, 30.02; H, 4.20; P, 12.81. Found: C, 30.33; H, 4.14; P, 12.56. Disulfide: mp 197–199 °C; ^{31}P NMR ($CDCl_3$) δ +110.3 and +62.0 (both d, $^3J_{PP}$ = 41.5). Anal. Calcd for $C_{10}H_{14}P_2S_2$: C, 46.16; H, 5.42; P, 23.81; S, 24.60. Found: C, 45.96; H, 5.50; P, 23.98; S, 24.20.

1,3,5,s*yn*-8-Tetramethyl-3a,4,7,7a-tetrahydro-4,7-phosphinidene-1-(*H*)-phosphindole (12). Reduction of 1.0 g (3.9 mmol) of **11**[18] gave 0.7 g (82%) of **12**, bp 80–83 °C (0.02 mm, Kugelrohr), as a clear oil: ^1H NMR $CDCl_3$) δ 1.29 (d, $^2J_{PH}$ = 3 Hz, PCH_3), 1.34 (d of d, J_{PH} = 3, and 2, PCH_3), 1.74 (s, CCH_3), 1.85 (s, CCH_3), 2.60–2.96 (m, —C*H*—, 3 H), 3.95–4.15 (m, —C*H*—, H-3a), 5.60 (d of d, $^2J_{PH}$ = 40, $^3J_{HH}$ = 6, —C*H*=, 1 H), 5.92 (b s, —C*H*=, 1 H); ^{13}C and ^{31}P NMR data, Table I. Bis(methiodide): mp 200–201 °C (lit.[63] 193–195 °C); ^{31}P NMR (D_2O) δ +94.6 and +55.4 (both d, $^3J_{PP}$ = 39.1). Disulfide: mp 231–235 °C; ^{31}P NMR ($CDCl_3$) δ +106.5 and +60.4 (both d, $^3J_{PP}$ = 41.5). Anal. Calcd for $C_{12}H_{18}P_2S_2$: C, 50.00; H, 6.30; P, 21.49; S, 22.21. Found: C, 49.81; H, 6.54; P, 21.36; S, 22.27.

1,3,3a,5,6,s*yn*-8-Hexamethyl-3a,4,7,7a-tetrahydro-4,7-phosphinidene-1(*H*)-phosphindole (16). Reduction of 2.0 g (7.0 mmol) of **15**[18] gave 1.7 g (96%) of **16** as a white solid: mp 77–80 °C; ^1H NMR ($CDCl_3$) δ 1.04 (d, $^2J_{PH}$ = 3 Hz, PCH_3, 6 H), 1.49 (s, CCH_3, 3 H), 1.65 (s, CCH_3, 3 H), 1.76 (s, CCH_3, 6 H), 2.10–2.60 (m, —C*H*—, 3 H), 5.40 (d of d, $^2J_{PH}$ = 40, $^3J_{HH}$ = 5, —C*H*=, 1 H); ^{13}C and ^{31}P NMR data, Table I. Disulfide: mp 158–159 °C; ^{31}P NMR ($CDCl_3$) δ +101.0 and +56.1 (both d, $^3J_{PP}$ = 49.0). Anal. Calcd for $C_{14}H_{22}P_2S_2$: C, 53.16; H, 7.01; P, 19.59; S, 20.24. Found: C, 53.24; H, 7.10; P, 19.29; S, 20.32.

1,s*yn*-8-Diphenyl-3a,4,7,7a-tetrahydro-4,7-phosphinidene-1(*H*)-phosphindole (10). From 700 mg (2.0 mmol) of **7**[18] was obtained 530 mg (83%) of **10** as a white solid: mp 124–127 °C; ^1H NMR ($CDCl_3$) δ 2.94–3.08 (m, —C*H*—, 1 H), 3.10–3.70 (m, —C*H*—, 2 H), 3.90–4.10 (m, —C*H*—, H-3a), 5.92 (d of d, $^2J_{PH}$ = 40, $^3J_{HH}$ = 5, —C*H*=, 1 H), 6.10–6.75 (m, —C*H*=, 3 H), 7.30 (m, Ar—*H*, 10 H). ^{13}C and ^{31}P NMR data, Table I. Disulfide: mp 181–183 °C (lit.[64] 183–184 °C); ^{31}P NMR δ +112.7 and +64.1 (both d, $^3J_{PP}$ = 44.0).

1,*syn*-8-Diphenyl-3,5-dimethyl-3a,4,7,7a-tetrahydro-4,7-phosphinidene-1(*H*)-phosphindole (14). Reduction of 1.0 g (2.6 mmol) of **13** gave 0.7 g (80%) of **14** as a sticky solid: ^1H NMR ($CDCl_3$) δ 1.47 (s, CCH_3, 3 H), 1.85 (s, CCH_3, 3 H), 2.70–3.20 (m, —C*H*—, 3 H), 3.85–4.20 (m, —C*H*—, 1 H), 5.0–6.0 (m, —C*H*=, 2 H), 6.80–7.75 (m, Ar—*H*, 10 H); ^{13}C and ^{31}P NMR data, Table I. Disulfide: mp 205–207 °C (lit.[65] mp 206 °C).

1,*syn*-12-Dimethyl-5b,5c,11,11a-tetrahydro-5c,11-phosphinidene-1-(*H*)-(tetrahydrobenzo[*b*]hexahydrobenzo[*e*])phosphindole (18). Reduction of 1.0 g (3.0 mmol) of **17**[66] gave 0.8 g (88%) of **18** as a clear oil: ^1H NMR ($CDCl_3$) δ 1.04 (d, $^2J_{PH}$ = 2 Hz, PCH_3, 3 H), 1.08 (d, $^2J_{PH}$ = 2, PCH_3, 3 H), 1.36–2.36 (m, —CH_2—, 16 H), 2.36–3.0 (m, —C*H*—, 2 H), 3.72–3.92 (m, —C*H*—, 1 H), 5.84 (br s, —C*H*=, 1 H); ^{31}P NMR ($CDCl_3$) δ +107.1 and +3.4 (both d, $^3J_{PP}$ = 24.4). Disulfide: mp 141–143 °C; ^{31}P NMR ($CDCl_3$) δ +112.0 and +61.1 (both d, $^3J_{PP}$ = 41.5). Anal. Calcd for $C_{18}H_{26}P_2S_2$: C, 58.69; H, 7.12; P, 16.82. Found: C, 58.59; H, 7.01; P, 16.68.

Reduction of Phosphole Oxide Dimers with Trichlorosilane. Dimer 5. A mixture of 1.0 g (4.3 mmol) of **5**, 2.0 g (14.8 mmol) of trichlorosilane, and 50 mL of benzene was refluxed for 2 h. After slow hydrolysis with excess 30% NaOH, the organic layer was separated, dried ($MgSO_4$), and concentrated to give 0.6 g (93%) of 1-methyl-3a,7a-dihydro-1(*H*)-phosphindole (6) as a clear oil: ^1H NMR ($CDCl_3$) δ 1.16 (d, $^2J_{PH}$ = 2, PCH_3), 2.80–3.10 (m, —C*H*, 1 H), 3.84–4.10 (m, —C*H*—, 1 H), 5.20–6.50 (m, —C*H*=, 6 H); ^{13}C NMR ($CDCl_3$) δ 14.3 (d, *J* = 23.9, PCH), 42.1 (d, *J* = 6.2, C-7a), 44.9 (d, *J* = 2.4, C-3a), 141.8 (d, *J* =

(59) Stothers, J. B.; Tan, C. T. *Can. J. Chem.* **1977**, *55*, 841.
(60) Stamm, E.; Lev, H. R.; Keese, R. *Helv. Chim. Acta* **1979**, *62*, 2174.
(61) Couffignal, R.; Kagan, H. B.; Mathey, F.; Samuel, O.; Santini, C. *C. R. Acad. Sci. Paris, Ser. C* **1980**, *291*, 29.
(62) Quin, L. D.; Bryson, J. G.; Moreland, C. G. *J. Am. Chem. Soc.* **1969**, *91*, 3308.
(63) Quin, L. D.; Borleske, S. G.; Engel, J. F. *J. Org. Chem.* **1973**, *38*, 1858.
(64) Märkl, G.; Potthast, R. *Tetrahedron Lett.* **1968**, 1755.
(65) Mathey, F.; Mankowski-Favelier, R. *Org. Magn. Reson.* **1972**, *4*, 171.
(66) Quin, L. D.; Mesch, K. A.; Orton, W. L. *Phosphorus Sulfur* **1982**, *12*, 161.

5.0, C-3), 121.0–132.6 (all d, 5C); ^{31}P NMR ($CDCl_3$) δ +11.7. The sulfide was prepared by adding 1 equiv of elemental sulfur to 1 equiv of **6** in pentane, giving an off-white solid, mp 84–87 °C; ^{1}H NMR ($CDCl_3$) δ 2.01 (d, $^2J_{PH}$ = 13, PCH_3), 3.20–3.56 (m, —CH—, 1 H), 3.90–4.30 (m, —CH—, 1 H), 5.60–7.0 (m, —CH=, 6 H); ^{31}P NMR ($CDCl_3$) δ +72.1. *m/e* Calcd for $C_9H_{11}PS$: 182.0319. Found: 182.0316.

Dimer 11. A mixture of 1.5 g (5.8 mmol) of **11**, 4.0 mL of trichlorosilane, and 50 mL of benzene was refluxed for 1.5 h. Treatment with 30% NaOH, followed by benzene extraction, gave 1.1 g (80%) of an oil which was primarily (90%) **12** by ^{31}P NMR analysis.

Dimer 13. To a benzene solution of phosphole dimer oxide **13** (1.5 g, 3.9 mmol) was added 5 mL of trichlorosilane, and the mixture then refluxed for 2 h. The organic layer after the usual NaOH treatment left 1.2 g (88%) of oil on evaporation, which had the ^{31}P NMR spectrum for the phosphole dimer **14**, containing a few percent of 3a,7a-dihydro-3,5-dimethyl-1-phenylphosphindole (tentative assignment based on δ ^{31}P NMR +27.5).

Reduction of Phosphole Oxide Dimers with Trichlorosilane–Triethylamine. Dimer 13. A mixture of 2.0 mL of trichlorosilane, 1.0 g of **13**, and 6.0 mL of triethylamine in 50 mL of benzene was refluxed for 1 h. Basification with 30% NaOH and extraction provided 0.3 g of a mixture shown by ^{31}P NMR analysis to consist of 60% of phosphole dimer **14** and 40% of (presumably) 3a,7a-dihydro-3,5-dimethyl-1-phenyldihydrophosphindole: δ(^{31}P) +27.5.

Dimer 11. In a similar experiment dimer **11** (1.0 g) was reduced to diphosphine **12** (34% yield); the only contaminant (5% by ^{31}P NMR analysis) was the anti isomer **20**.

Reduction of Phosphole Oxide Dimers with Phenylsilane. A solution of 1.0 g (4.4 mmol) of dimer **5**, 2.0 g (18.8 mmol) of phenylsilane and 25 mL of benzene was refluxed for 16 h and then hydrolyzed with excess 30% NaOH. The organic layer was separated, dried ($MgSO_4$), and concentrated to give 0.55 g of a slightly yellow oil. ^{31}P NMR analysis indicated a mixture of **9** (25%), **19** (65%), and ö (10%, δ(^{31}P) ($CDCl_3$) +11.7).

The same procedure was used for dimer **11** (1.0 g (3.9 mmol), 2.0 g (18.8 mmol) of phenylsilane, and 50 mL of benzene), yielding 0.6 g (68%) of a mixture of **12** (27%), **20** (67%), and 3a,7a-dihydro-1,3,5-trimethylphosphindole (6%, δ(^{31}P) ($CDCl_3$) +10.6).

For dimer **13**, a mixture of 1.0 g (2.6 mmol) and 2.0 g (18.8 mmol) of phenysilane in 40% mL of benzene was refluxed for 24 h, yielding 0.5 g (58%) of a mixture of **14** (8%), **58** (72%), and 3a,7a-dihydro-3,5-dimethyl-1-phenylphosphindole (20%, assignment from δ(^{31}P) ($CDCl_3$) +27.5).

Syn to Anti Conversion of Phosphole Dimers. 1,*anti*-8-Dimethyl-3a,4,7,7a-tetrahydro-4,7-phosphinidene-1(*H*)-phosphindole (19). A solution of 162 mg (0.82 mmol) of phosphole dimer **9** and 5 drops of methanol in a small amount of $CDCl_3$ was placed in a 5-mm NMR tube and warmed to 50 °C in the NMR probe. The reaction was complete after 5 h to give a 3:1 mixture of **19** (δ ^{31}P NMR ($CDCl_3$) +30.2 and −7.9, $^3J_{PP} \sim 0$) and dihydrophosphindole **6** (δ(^{31}P) +11.7).

The bis(methiodide) was prepared in pentane and recrystallized from methanol to give the same methiodide prepared from **9**; mp 198–199 °C.

1,3,5,*anti*-8-Tetramethyl-3a,4,7,7a-tetrahydro-4,7-phosphinidene-1-(*H*)-phosphindole (20). A solution of 1.4 g (6.3 mmol) of phosphole dimer **12** and 15 mL of methanol was warmed at 50 °C for 4.5 h and then concentrated and distilled to give 1.1 g (78%) of **20** as a clear oil: bp 81–83 °C (0.03 mm); ^{1}H NMR ($CDCl_3$) δ 1.00 (d, $^2J_{PH}$ = 5, PCH_3), 1.16 (d, $^2J_{PH}$ = 3, PCH_3), 1.76 (d, CCH_3), 1.96 (s, CCH_3), 2.57–3.05 (m, —CH—, 3 H), 3.82–4.22 (m, —CH—, H-3a), 5.33–6.20 (m, —CH=, 2 H); ^{13}C and ^{31}P NMR data, Table I. Bis(methiodide): mp 200–201 °C, identical with that from **12**. Disulfide: mp 225–226.5 °C; ^{31}P NMR ($CDCl_3$) δ +104.4 and +63.1 (both d, ^3J = 36.6). Anal. Calcd for $C_{12}H_{18}P_2S_2$: C, 50.00; H, 6.30; P, 21.49; S, 22.21. Found: C, 50.14; H, 6.38; P, 21.38; S, 22.42. A sample of dimer **12** left standing for 1 month in C_6D_6 was also completely rearranged to **20**.

1,*anti*-8-Diphenyl-3,5-dimethyl-3a,4,7,7a-tetrahydro-4,7-phosphinidene-1(*H*)-phosphindole (21). A solution of 1.7 g (4.9 mmol) of phosphole dimer **14** and 15 mL of methanol was warmed at 50 °C for 4 h and then concentrated until the product began to crystallize. The mixture was cooled to 0 °C. The precipitate was filtered and recrystallized from methanol to give 1.0 g (59%) of **21** as white crystals: mp 132–134 °C; ^{1}H NMR ($CDCl_3$) δ 1.82 (s, CCH_3), 1.92 (s, CCH_3), 2.80–3.80 (m, —CH—, 4 H), 5.59 (d, $^2J_{PC}$ = 40, —CH=, 1 H), 6.20 (br s, —CH=, 1 H), 7.20–7.60 (m, Ar—H, 10 H); ^{13}C and ^{31}P NMR data, Table I.

1,*anti*-8-Diphenyl-3a,4,7,7a-tetrahydro-4,7-phosphinidene-1(*H*)-phosphindole (22). A solution of 200 mg (0.63 mmol) of phosphole dimer **10** and 10 mL of methanol was warmed at 50 °C for 4 h. The mixture was cooled to 0 °C and filtered to give 120 mg (60%) of **22** as white crystals: mp 161–163 °C; ^{1}H NMR ($CDCl_3$) δ 2.84–3.08 (m, —CH—, 1 H), 3.08–3.70 (m, —CH—, 2 H), 3.94–4.08 (m, —CH, H-3a), 5.70–6.76 (m, —CH=, 4 H), 7.30 (br s, Ar—H, 10 H); ^{13}C and ^{31}P NMR data, Table I. Disulfide: mp 217–218 °C; ^{31}P NMR ($CDCl_3$) +106.5 and +75.7 (both d, $^3J_{PP}$ = 34.1). Anal. Calcd for $C_{20}H_{18}P_2S_2$: C, 62.50; H, 4.72. Found: C, 62.11; H, 4.75.

Characterization of 3a,7a-Dihydro-1,3,5-trimethylphosphindole. To a flame-dried reaction vessel was added 0.94 g (9.2 mmol) of freshly distilled phosphole dimer **12** in 40 mL of dry xylene. After 16.5 h at 121–131 °C, the clear solution was concentrated (high vacuum) to yield a cloudy oil. The oil was Kugelrohr-distilled at 60–62 °C (0.12 mm) to give 0.5 g (67%) of the dihydrophosphindole: ^{1}H NMR ($CDCl_3$) δ 1.10 (d, $^2J_{PH}$ = 2.6, PCH_3), 1.7 (s, CCH_3), 1.81 (apparent t, CCH_3), 2.4–3.1 (m, CH), 5.2–6.0 (m, vinyl CH=); ^{13}C NMR ($CDCl_3$) δ 18.0 (J_{PC} = 3.3, 3-CH_3), 21.6 (5-CH_3), 43.7 (J_{PC} = 4.4, C-7a), 48.2 (C-3a), 118.0 (J_{PC} = 4.4, C-4), 125.0 (J_{PC} = 11.0), C-6 or C-7), 125.3 (J_{PC} = 14.3, C-6 or C-7), 128.0 (J_{PC} = 16.5, C-2), 151.2 (J_{PC} = 5.5, C-3); ^{31}P NMR ($CDCl_3$) δ +11.0. Some unchanged **12** was also present.

Addition of methyl iodide in pentane caused immediate cloudiness to develop. The solution was stored in the freezer for 2 days, and the white solid was then filtered and washed with pentane. This was recrystallized from methanol–ethyl acetate to yield a solid containing mainly the salt of the dihydrophosphindole. The solid was stirred in $CHCl_3$ and filtered; the filtrate was concentrated under vacuum to yield a white solid. This was recrystallized from methanol–ethyl acetate to yield 0.041 g (5%) of the methiodide of 3a,7a-dihydro-1,3,5-trimethylphosphindole: mp 187.5–189.5 °C; ^{13}C NMR (Me_2SO-d_6) δ 8.5 (J_{PC} = 50.5, PCH_3), 9.7 (J_{PC} = 50.5, P–CH_3), 19.0 (J_{PC} = 16.5, 3-CH_3), 20.9 (5-CH_3), 33.7 (J_{PC} = 50.5, C-7a), 47.7 (J_{PC} = 6.6, C-3a), 109.2 (J_{PC} = 80.2, C-2), 117.0 (J_{PC} = 3.3, C-7 or C-4), 118.2 (J_{PC} = 8.8, C-7 or C-4), 129.1 (J_{PC} = 17.6, C-6), 129.2 (C-5), 172.3 (J_{PC} = 25.3, C-3); ^{31}P NMR (Me_2SO-d_6) δ +59.5. Anal. Calcd for $C_{12}H_{18}IP$: C, 45.02; H, 5.67; P, 9.67. Found: C, 44.94; H, 5.64; P, 9.77.

9-Phenyl-9-phosphatricyclo[4.2.1.0^{2,5}]nona-3,7-diene 9-Oxide (24). This compound was prepared from the bicyclo[4.2.1]nonatriene **23** by the method of Turnblom and Katz:[24] mp 175–177 °C (lit.[24] mp 178–179 °C); ^{13}C NMR ($CDCl_3$) δ 41.05 (d, $^2J_{PC}$ = 30.5, C-2, C-5), 41.79 (d, $^1J_{PC}$ = 62.0, C-1, C-6); ^{31}P NMR ($CDCl_3$) δ +98.8.

9-Phenyl-9-phosphatricyclo[4.2.1.0^{2,5}]nona-3,7-diene (26). To 2.0 g (14.8 mmol) of trichlorosilane and 4.4 g (44.4 mmol) pyridine in 50 mL of benzene was added 500 mg (2.2 mmol) of **24**. The mixture was refluxed for 2 h and then cooled in an ice–water bath for hydrolysis with excess 30% NaOH. The layers were separated, and the organic layer was dried ($MgSO_4$) and concentrated to give 400 mg (80%) of **26** as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 2.65 (d of m, $^3J_{PH}$ = 15.0, —CHCH—), 3.13 (d, $^2J_{PH}$ = 3, PCH—), 5.70 (s, —CH=CH—), 5.96 (m, —CH=CH—), 7.08 (m, Ar—H); ^{13}C and ^{31}P NMR data, Table I. This product was oxidized with 10% H_2O_2 to give a compound identical with **24**: mp 174–176 °C.

Reduction of 24 with Trichlorosilane. To a solution of 704 mg (3.1 mmol) of **24** and 15 mL of benzene was added 1.0 mL of trichlorosilane. The mixture was stirred at room temperature overnight and then hydrolyzed with excess 30% NaOH. The organic phase was dried ($MgSO_4$) and concentrated to give 400 mg of a mixture consisting only of cyclooctatetraene, ^{1}H NMR ($CDCl_3$) δ 5.28 (s, —CH=), and phenylphosphine, ^{1}H NMR ($CDCl_3$) δ 3.64 (d, $^1J_{PH}$ = 195 Hz, —PH_2), 6.77 (br s, Ar—H); ^{31}P NMR ($CDCl_3$) δ −123.0.[67]

The reduction was repeated with only 1 molar equiv of trichlorosilane. In a 5-mm NMR tube were placed 168 mg (0.74 mmol) of **24**, 0.5 mL of benzene-d_6 and 99 mg (0.74 mmol) of trichlorosilane. The mixture was warmed at 55 °C for 15 min and its spectra were measured: ^{1}H NMR (C_6D_6) δ 5.30 (s, —CH= of cyclooctatetraene) and 3.70 (d, $^1J_{PH}$ = 200 Hz, —PH_2 of phenylphosphine), 6.80 (m, Ar—H); ^{31}P NMR (C_6D_6) δ −124.1 (phenylphosphine) and +161.6 [bis(trichlorosiloxy)-phenylphosphine (**28**)].

Reaction of Phosphine 26 with Methanol. A mixture of 200 mg (0.9 mmol) of **26** and 200 mg (4.3 mmol) of methanol in $CDCl_3$ was warmed in a 5-mm tube to 50 °C for 15 min. Spectra showed only cyclooctatetraene (^{1}H NMR ($CDCl_3$) δ 5.3), phenylphosphine (^{31}P NMR ($CDCl_3$) −123.0), and dimethyl phenylphosphonite (^{1}H NMR ($CDCl_3$), δ 3.40 (d, $^3J_{PH}$ = 11 Hz, $POCH_3$), 6.80–7.55 (m, Ar—H); ^{31}P NMR ($CDCl_3$) δ +160.4 (lit.[69] δ +162). No **26** remained.

1,4,*syn*-7-Triphenyl-7-phosphabicyclo[2.2.1]hept-5-ene-2-carbonitrile 7-Oxide (30). Cycloaddition according to Campbell et al.[28] of 1,2,5-

(67) Several values have been reported in the range −119 to −124: Maier, L. In "Organic Phosphorus Compounds"; Kosolapoff, G. M., Maier, L., Eds.; Wiley: New York, 1972; Vol. I, p 111.

(68) Van Wazer, J. R.; Callis, C. F.; Shoolery, J. N.; Jones, R. C. *J. Am. Chem. Soc.* **1956**, *78*, 5715.

(69) Baudler, M.; Carlsohn, B.; Böhm, W.; Reuschenbach, G. *Z. Naturforsch., B* **1976**, *31B*, 558.

triphenylphosphole oxide and acrylonitrile gave **30** (95%) as a white powder: mp 174.6–176.6 °C (lit.[28] mp 180 °C); ^{1}H NMR (250 MHz using a Bruker WM250 spectrometer, $CDCl_3$) δ 2.28 (d of d of d, $^3J_{PH_1}$ = 24.6, $^2J_{H_1H_2}$ = 12, $^3J_{H_1H_3}$ = 4.4, H_1), 3.53 (d of t, $^3J_{PH_2}$ = 1.5, $^2J_{H_2H_1}$ = 12, $^3J_{H_2H_3}$ = 10, H_2), 4.23 (d of d, $^3J_{H_3H_1}$ = 4.4, $^3J_{H_3H_2}$ = 10, *H*CCN), 6.97 (m, C*H*=C*H*), 7.2–7.6 (m, Ar—*H*); partial ^{13}C NMR ($CDCl_3$) δ 36.2 (d, $^2J_{PC}$ = 22.3, PC*C*H$_2$), 39.7 (d, $^2J_{PC}$ = 9.7, PC*C*CN), 56.2 (d, $^1J_{PC}$ = 62.4, bridgehead P*C*), 58.7 (d, $^1J_{PC}$ = 65.4, bridgehead P*C*), 119.4 (s, *C*CN); ^{31}P NMR ($CDCl_3$) δ +75.5.

1,4,*syn*-7-Triphenyl-7-phosphabicyclo[2.2.1]hept-5-ene-2-carbonitrile (32). Two grams (5.2 mmol) of **30** was reduced with Cl_3SiH–pyridine by the conditions used for phosphole oxide dimers to yield 1.3 g (68%) of a mixture of phosphine **32**, $(C_6H_5P)_4$, $(C_6H_5P)_5$, and 1,2-dihydro-3,6-diphenylbenzonitrile. Attempts to purify crude **32** by recrystallization, column chromatography, and derivatization with methyl iodide were unsuccessful. ^{31}P NMR ($CDCl_3$) of mixture: δ +129.7 (**32**, 15%), −47.9 ($(C_6H_5P)_4$,[69] 75%), −4.2 ($(C_6H_5P)_5$,[69] 10%).

One gram of the crude mixture was oxidized with 10% H_2O_2 in a $CHCl_3$–H_2O medium to yield 0.8 g of a mixture of crude yellow solid consisting of oxide **30** (δ(^{31}P) +75.9), and phenylphosphinic acid, δ(^{31}P) ($CDCl_3$) +22.2, $^1J_{PH}$ = 576 (lit.[68] +23 (H_2O), $^1J_{PH}$ = 576 Hz).

1,4,*syn*-7-Triphenyl-7-phosphabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic Anhydride 1-Oxide (31). Maleic anhydride and 1,2,5-triphenylphosphole 1-oxide[28] gave 96% of **31**: mp 228.6–230.6 °C (lit.[28] mp 229–231 °C); ^{1}H NMR (Me_2SO-d_6) δ 3.3 (s, C*H*, 2 H), 7.2–7.7 (m, C*H*=C*H* and Ar—*H*, 17 H); ^{31}P NMR (Me_2SO-d_6) δ +85.6.

Dimethyl 1,4,*syn*-7-Triphenyl-7-phosphabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate 7-Oxide (34). The diester **34** was prepared from anhydride **31** by methanolysis with MeOH–H_2SO_4 by the method of Schmidt.[39] Yields ranged from 57% to 90% in several preparations: mp 189–190.5 °C (lit.[39] mp 187–188 °C); ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.46 (s, CO_2CH_3), 4.66 (d, $^3J_{PH}$ = 1.8, *HCCH*), 6.98 (d, $^3J_{PH}$ = 11.8, C*H*=C*H*), 7.1–7.6 (m, Ar—*H*); ^{13}C NMR ($CDCl_3$) δ 51.7 (s, CO_2CH_3), 54.8 (d, $^2J_{PC}$ = 13.7, *C*H), 58.6 (d, $^1J_{PC}$ = 65.4, bridgehead P*C*), 170.2 (s, $^3J_{PC}$ = 15.6, *C*O$_2$CH$_3$); ^{31}P NMR ($CDCl_3$) δ +74.5.

Dimethyl 1,4,*syn*-7-Triphenyl-7-phosphabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (35). Reduction of 0.5 g (1.0 mmol) of **34** with Cl_3SiH–pyridine as before gave 0.3 g (62%) of a white solid, shown by ^{1}H and ^{31}P NMR analysis to be a 4:1:8 mixture of **35**, $(C_6H_5P)_{4-5}$, and dimethyl 1,2-dihydro-3,6-diphenylphthalate. Separation of this mixture by recrystallization or column chromatography was unsuccessful, and it was used for spectral characterization of **35**: ^{1}H NMR ($CDCl_3$) δ 3.41 (s, CO_2CH_3), 4.45 (d, $^3J_{PH}$ = 4.6, C*H*CO$_2$), 6.78 (s, C*H*=C*H*), 6.8–7.5 (m, Ar—*H*); partial ^{13}C NMR ($CDCl_3$) δ 51.5 (s, O*C*H$_3$), 56.6 (d, $^2J_{PC}$ = 32.2, *C*HCO$_2$), 64.6 (d, $^1J_{PC}$ = 8.1, bridgehead P*C*), 170.3 (s, —*C*O$_2$); ^{31}P NMR ($CDCl_3$) δ +137.0. Attempted derivatization of **35** as the methyl iodide salt gave only complex mixtures. The crude phosphine mixture was oxidized with 10% H_2O_2 in $CHCl_3$–H_2O to yield 0.3 g (11% from the starting oxide) of **34**: ^{31}P NMR ($CDCl_3$) δ +75.1.

3,6,7,9-Tetramethyl-3,9-diphosphapentacyclo[5.3.0.0^{2,6}.0^{4,10}.0^{5,8}]decane (38). One gram (3.9 mmol) of **37** [prepared by photolysis of **11** as described[18] (^{31}P NMR ($CDCl_3$) δ +71.3)] was reduced with Cl_3SiH–pyridine by conditions given in the general method to yield 0.4 g (46%) of **38** as a light-yellow oil: ^{1}H NMR ($CDCl_3$) δ 0.85 (s, PCH_3, 6 H), 1.20 (s, CCH_3, 6 H), 2.40–2.90 (m, C*H*, 6 H); ^{13}C NMR ($CDCl_3$) δ 4.8 (apparent t, X of AA′X, PCH$_3$), 17.1 (s, C*C*H$_3$), 41.7 (t, *C*H), 46.9 (t, *C*H), 48.8 (t, *C*H), 53.1 (s, *C*CH$_3$); ^{31}P NMR ($CDCl_3$) δ −1.8. The diphosphine was reacted in pentane with excess methyl iodide for 4 days at −18 °C. The crystalline precipitate was filtered and washed with pentane, yielding 0.9 g (99%) of the bis(methiodide) which decomposed over a wide range: ^{1}H NMR (DDS–D_2O) δ 1.33 (s, CCH_3, 6 H), 1.99 (d, $^2J_{PH}$ = 11.0, PCH_3, 6 H), 2.17 (d, $^2J_{PH}$ = 11.7, PCH_3, 6 H), 3.5 (br m, PCC*H*, 2 H), 3.75 (m, PC*H*, 4 H); ^{13}C NMR (D_2O with CH_3OH as internal reference) δ 2.9 (apparent t, P*C*H$_3$), 4.5 (apparent t, PCH$_3$), 14.4 (s, *C*CH$_3$), 36.7 (t, *C*H), 40.0 (t, *C*H), 44.0 (t, *C*H), 50.0 (t, *C*CH$_3$); ^{31}P NMR (D_2O) δ +64.7. Anal. Calcd for $C_{14}H_{24}I_2P_2$: C, 33.10; H, 4.76; P, 12.19. Found: C, 32.99; H, 4.90; P, 12.04. Diphosphine **38** was also obtained as the only product in the phenylsilane reduction using the conditions described for phosphole oxide dimers.

The reduction was also performed with trichlorosilane in the absence of pyridine. To a suspension of 1.0 g (3.9 mmol) of **37** in 50 mL of benzene was added 3.0 mL of Cl_3SiH (29 mmol) dropwise (5 min). A mild exotherm occurred. The solution was refluxed for 1.5 h before hydrolysis with excess 30% NaOH in an ice–water bath. The layers were separated and the aqueous layer extracted with two 25-mL portions of benzene. The combined benzene layers were dried over $MgSO_4$. Gravity filtration and concentration in vacuo yielded 0.4 g (46%) of a 1:1 mixture of **39** (δ(^{31}P) −15.1 and −17.2, $J_{PP} \sim 0$) and **38** (δ(^{31}P) −1.9) as a light-yellow oil that formed the same methiodide as provided by pure **38**, δ(^{31}P) (D_2O) +64.7. Heating a solution of **38** in xylene at 130 °C for 24 h caused isomerization of about half the sample to a diphosphine with the same NMR properties found for **39**. In other reductions of **37** using similar conditions only **38** was obtained.

1,*syn*-8-Dimethyl-2,3,3a,4,5,6,7,7a-octahydro-4,7-phosphinidene-1-(*H*)-phosphindole (41). A mixture of 2.0 g (9.0 mmol) of **40**,[18] 5.0 g (37 mmol) of trichlorosilane, and 20 mL of benzene was heated at reflux for 1.5 h and then hydrolyzed with excess 20% NaOH. The organic layer was dried over $MgSO_4$ and concentrated to give 0.5 g (32%) of **41** as a clear oil: ^{1}H NMR ($CDCl_3$) δ 0.85 (d, $^2J_{PH}$ = 3, PCH_3), 0.87 (d, $^2J_{PH}$ = 2, PCH_3), 1.0–3.15 (m, −CH_2−, −C*H*−, 12 H); ^{13}C NMR ($CDCl_3$) δ 4.8 (d of d, $^1J_{CP\text{-}8}$ = 27.9, $^4J_{CP\text{-}1}$ = 1.2, CH_3P-8), 10.6 (d, $^1J_{CP\text{-}1}$ = 15.9, CH_3P-1), 21.2 (d, $^2J_{CP\text{-}8}$ = 5.4, C-5), 22.9 (d of d, $^2J_{CP\text{-}8}$ = 4.8, $^3J_{CP\text{-}1}$ = 15.9, C-6), 28.9 (d of d, $^4J_{CP\text{-}8}$ = 1.2, $^1J_{CP\text{-}1}$ = 10.4, C-2), 30.4 (d of d, $^3J_{CP\text{-}8}$ = 4.8, $^2J_{CP\text{-}1}$ = 10.4, C-3), 42.7 (d of d, $^1J_{CP\text{-}8}$ = 8.6, $^2J_{CP\text{-}1}$ = 15.8, C-7), 44.6 (d, $^1J_{CP\text{-}8}$ = 7.2, C-C), 45.1 (d of d, $^2J_{CP\text{-}8}$ = 22.7, $^2J_{CP\text{-}1}$ = 3.6, C-3a), 49.4 (d of d, $^2J_{CP\text{-}8}$ = 18.9, $^1J_{CP\text{-}1}$ = 12.3, C-7a); ^{31}P NMR, Table II.

The bis(methiodide) prepared in pentane and recrystallized from methanol had a melting point of 325–326 °C; ^{31}P NMR ($CDCl_3$) δ +58.3 and +52.5 (both d, $^3J_{PP}$ = 46.4). Anal. Calcd for $C_{12}H_{24}I_2P_2$: C, 29.77; H, 5.00; P, 12.80. Found: C, 29.63; H, 5.18; P, 12.96.

9-Phenyl-9-phosphatricyclo[4.2.1.0^{2,5}]nonane 9-Oxide (42). This compound was prepared by hydrogenation of oxide **24** according to Turnblom and Katz[24] in 73% yield after sublimation at 135 °C (0.05 mm): mp 150–152 °C (lit.[24] mp 152–154 °C); ^{31}P NMR ($CDCl_3$) δ +67.0.

9-Phenyl-9-phosphatricyclo[4.2.1.0^{2,5}]nonane (43). To a solution of 650 mg (2.8 mmol) of **42** and 15 mL of benzene was added 1.0 g (7.4 mmol) of trichlorosilane. The mixture was allowed to stir at room temperature overnight and then hydrolyzed carefully with excess 20% NaOH. The organic phase was separated, dried over $MgSO_4$, and concentrated to give 5.20 mg (93%) of **43** as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 1.70–3.00 (m, −CH_2− and −C*H*−), 7.12–7.70 (m, Ar-*H*); ^{31}P NMR ($CDCl_3$) δ +22.0. This product was oxidized with 10% H_2O_2 to give **42**: mp 153–154 °C.

***syn*-8-Methyl-8-phosphabicyclo[3.2.1]oct-6-ene 8-Oxide (44) and *anti*-8-Methyl-8-phosphabicyclo[3.2.1]oct-6-ene 8-Oxide (46).** The procedure used was similar to that reported.[30] To a brown bottle containing 0.1 g of copper stearate was added 10.0 g (0.11 mol) of 1,3-cycloheptadiene and 14.1 g of methylphosphonous dichloride under N_2. The bottle was sealed with a Teflon lid and stored for 3 months in the dark. The white solid cycloadduct was hydrolyzed in ice water. Chloroform (100 mL) was added and the pH adjusted to approximately 6 with solid $NaHCO_3$. The mixture was filtered and the layers separated. The aqueous layer was extracted with four 25-mL portions of $CHCl_3$. The organic layers were combined and dried over Na_2SO_4 and $MgSO_4$. Concentration by rotoevaporation and removal of residual solvent by high vacuum gave 14.4 g (84%) of a 5:1 mixture of **46** and **44**. If the cycloaddition was performed in pentane, the yield was only 10% and the **46**:**44** ratio was 2:1. Pure **46** was obtained by column chromatography as described[30] and gave the reported ^{1}H NMR spectrum: ^{13}C NMR ($CDCl_3$) δ 9.9 (d, $^1J_{PC}$ = 56.8, PCH_3), 17.1 (d, $^2J_{PC}$ = 4.9, probably PC*C*H$_2$), 22.9 (s, probably PCC*C*H$_2$), 39.6 (d, $^1J_{PC}$ = 61.0, bridgehead P*C*), 129.5 (d, $^2J_{PC}$ = 7.3, PC*C*=); ^{31}P NMR ($CDCl_3$) δ +73.7. Spectra of **44** were obtained on a 1:2 mixture with **46**; partial ^{13}C NMR ($CDCl_3$) δ 18.4 (d, $^2J_{PC}$ = 5.5, probably PC*C*H$_2$), 18.8 (d, $^3J_{PC}$ = 2.2, probably PCC*C*H$_2$—), 36.1 (d, $^1J_{PC}$ = 60.4, bridgehead P*C*), 129.7 (d, $^2J_{PC}$ = 14.3, PC*C*=); ^{31}P NMR ($CDCl_3$) δ +69.4.

***anti*-8-Methyl-8-phosphabicyclo[3.2.1]oct-6-ene (47).** One gram (6.4 mmol) of **46**, obtained from column chromatography of a mixture with **44** as reported[30] was reduced by the general procedure used for phosphole oxide dimers to yield 0.6 g (67%) of **47** as a white solid: ^{1}H NMR ($CDCl_3$) δ 1.12 (d, $^2J_{PH}$ = 4.1, PCH_3), 1.2–2.0 (m, PCHCH_2CH_2), 2.23 (d of m, PC*H*), 6.13 (d of m, C*H*=C*H*); ^{31}P and ^{13}C NMR data, Table I. This phosphine was converted to the methiodide (also see next section) by addition of excess iodomethane to a pentane solution: ^{31}P NMR ($CDCl_3$) δ +60.1.

Reductions of 44 and 46 with Trichlorosilane. One gram (6.4 mmol) of a 2:1 mixture of **46** and **44** was reduced with trichlorosilane–pyridine by the general procedure to yield 0.5 g of light yellow oil (56%), a 2:1 mixture of **47** and **45** as determined by ^{31}P NMR. Spectra for **45** were obtained on this mixture: ^{1}H NMR ($CDCl_3$) δ 0.99 (d, $^2J_{PH}$ = 3.3, PCH_3), 1.2–2.0 (m, PCHCH_2CH_2), 2.2 (d of m, PC*H*), 5.90 (m, C*H*CH); ^{31}P and ^{13}C NMR data, Table I.

The phosphine mixture gave a single methiodide salt (91%, dec over a wide range) by adding excess methyl iodide to a pentane solution: ^{1}H NMR (DDS–D_2O) δ 1.74 (d, $^2J_{PH}$ = 12, PCH_3), 1.6–2.0 (m, PCHCH_2CH_2), 1.97 (d, $^2J_{PH}$ = 12, PCH_3), 3.0–3.3 (m, PC*H*), 6.31 (d of m, C*H*=C*H*); ^{13}C NMR (D_2O with CH_3OD as internal reference, δ 49.0) δ 4.5 (d, $^1J_{PC}$ = 49.4, P*C*H$_3$), 4.8 (d, $^1J_{PC}$ = 45.0, P*C*H$_3$), 17.7 (d, $^3J_{PC}$ = 6.6, probably PCC*C*H$_2$), 19.5 (d, $^2J_{PC}$ = 2.2, PC*C*H$_2$), 34.3 (d,

$^1J_{PC}$ = 50.5, bridgehead PC), 130.4 (d, $^2J_{PC}$ = 9.9, PCC=); ^{31}P NMR (D_2O) δ +60.0. Anal. Calcd for $C_9H_{16}IP$: C, 38.32; H, 5.72; P, 10.98. Found: C, 38.11; H, 5.80; P, 10.86.

The reduction was performed also in the absence of pyridine, giving the same 2:1 mixture (67% yield) of **47** and **45**.

Reduction of 46 with Si_2Cl_6. To a solution of 2.8 g (10.4 mmol) of Si_2Cl_6 in 50 mL of benzene was added 1.4 g (9.0 mmol) of **46** in one portion. The solution was refluxed for 1.5 h before hydrolysis with 30% NaOH. The phases were separated and the aqueous layer extracted with two 20-mL portions of benzene. The organic phases were combined and dried over $MgSO_4$. Rotoevaporation gave 0.2 g of a 1.3:1 mixture by ^{31}P NMR ($CDCl_3$) of original oxide **46** (δ +37.6) and phosphine **47** (δ −17.8).

Reduction of 46 with Phenylsilane. A mixture of 0.1 g (0.64 mmol) of pure oxide **46** and 0.2 g (1.85 mmol) of phenylsilane was stirred at room temperature for 11 h. The ^{31}P NMR spectrum taken directly on the reaction mixture showed that the main product was phosphine **47** (δ −17.6) with a few percent of the syn isomer (**45**) at δ +50.0. Methylphosphine was observed at δ −160.7 (lit.[69] δ −163.5).

***syn*-9-Methyl-9-phosphabicyclo[4.2.1]non-7-ene 9-Oxide (48) and *anti*-9-Methyl-9-phosphabicyclo[4.2.1]non-7-ene 9-Oxide (49).** To a flame-dried reaction vessel was added 20.0 g (0.18 mol) of 1,3-cyclooctadiene, 0.1 g of copper stearate, and 21 g (0.18 mmol) of methylphosphonous dichloride. The vessel was sealed under Ar and heated at 119–120 °C for 2 weeks to yield a dark solution with a thick black oil on the bottom of the vessel. On cooling, fine white crystals precipitated out of the solution. The liquid was poured into 50 mL of cold water. The thick black solid remaining in the vessel was dissolved in $CHCl_3$ and added to the cold water. The solution was taken to a pH of approximately 6 with solid $NaHCO_3$. The mixture was filtered and the layers separated. The aqueous layer was extracted with five 20-mL portions of $CHCl_3$. The combined $CHCl_3$ layers were dried over Na_2SO_4 and $MgSO_4$. Concentration by rotoevaporation and removal of residual solvent by high vacuum yielded 1.2 g (4%) of 4.5:1 mixture by ^{31}P NMR analysis of **48** and **49** as an off-white solid. Repeated recrystallization of the mixture yielded pure **48** as a white solid: mp 106.8–107.8 °C; ^{1}H NMR ($CDCl_3$) δ 1.53 (d, $^2J_{PH}$ = 12.3, $^2J_{HH}$ = 2.9, PC*H*), 6.01 (d of m, $^3J_{PH}$ = 24.3, C*H*=C*H*); ^{13}C NMR ($CDCl_3$) δ 13.0 (d, $^1J_{PC}$ = 64.5, P*C*H$_3$), 25.2 (d, $^2J_{PC}$ = 2.9, probably PC*C*H$_2$), 27.7 (s, $^3J_{PC}$ = 0, probably PCC*C*H$_2$), 38.7 (d, $^1J_{PC}$ = 62.5, bridgehead P*C*), 132.9 (d, $^2J_{PC}$ = 16.6, PC*C*=); ^{31}P NMR ($CDCl_3$) δ +64.4. Anal. Calcd for $C_9H_{15}OP$: C, 63.52; H, 8.88; P, 18.20. Found: C, 63.43; H, 8.82; P, 17.96.

Pure **49** could not be obtained from the recrystallization. Its spectra were obtained on a 1:1 mixture of **48** and **49**: ^{1}H NMR ($CDCl_3$) δ 1.84 (d, $^2J_{PH}$ = 12.5, PCH_3), 1.5–2.2 (m, PCCH_2CH_2), 2.3–3.1 (m, PC*H*), 5.6–6.4 (m, C*H*=C*H*); ^{13}C NMR ($CDCl_3$) δ 12.4 (d, $^1J_{PC}$ = 56.8, P*C*H$_3$), 24.8 (d, $^2J_{PC}$ = 1.2, probably PC*C*H$_2$), 26.4 (d, $^3J_{PC}$ = 4.3, PCC*C*H$_2$), 42.6 (d, $^1J_{PC}$ = 61.0, bridgehead P*C*), 133.6 (s, $^2J_{PC}$ = 0, PC*C*=); ^{31}P NMR ($CDCl_3$) δ +67.6.

***syn*-9-Methyl-9-phosphabicyclo[4.2.1]non-7-ene (50).** Reduction of 0.2 g (1.2 mmol) of **48** with Cl_3SiH–pyridine by the phosphole oxide dimer procedure gave 0.1 g (54%) of **50** as a clear oil: ^{1}H NMR ($CDCl_3$) δ 0.93 (d, $^2J_{PH}$ = 3.3, PC*H*$_3$), 1.4–2.0 (m, PCHCH_2CH_2), 2.4–2.6 (m, PC*H*), 5.79 (d of d, *J* = 4.7, *J* = 2.4, C*H*=C*H*); ^{31}P and ^{13}C NMR data, Table I. The phosphine was unusually sensitive to oxidation, which interfered with quaternization. The phosphine was quaternized in pentane with methyl iodide; the solution became cloudy immediately and was stored overnight in the freezer. The solvent was removed in vacuo to give 0.2 g of **50** containing about 20% of oxidation product **48**. No separation was effected by recrystallization and spectra for the salt were recorded on the mixture: ^{13}C NMR ($CDCl_3$) δ 8.3 (d, $^1J_{PC}$ = 48.2, P-*C*H$_3$), 8.7 (d, $^1J_{PC}$ = 48.8, P*C*H$_3$), 24.7 (d, $^2J_{PC}$ = 2.4, PC*C*H$_2$ or PCC*C*H$_2$), 27.0 (s, $^3J_{PC}$ = O, PCCH$_2$ or PCCC*H*$_2$), 38.5 (d, $^1J_{PC}$ = 48.8, bridgehead P*C*), 132.6 (d, $^2J_{PC}$ = 11.6, PC*C*=); ^{31}P NMR ($CDCl_3$) δ +50.6.

Reduction of a Mixture of 48–49 with $HSiCl_3$–Pyridine. A 1:1 mixture of the oxides **48** and **49** (0.1 g, 0.59 mmol) was reduced by the general procedure, yielding 0.09 g (99%) of a mixture of **50** and **51** as a clear oil, used for procuring ^{1}H and ^{13}C NMR signals of **51**: ^{31}P and ^{13}C NMR data, Table I.

The mixture of phosphines was then taken up in 20 mL of $CHCl_3$ and oxidized with 3 mL of 10% H_2O_2 by vigorous stirring for 0.75 h. The layers were separated, and the aqueous layer was extracted with three 10-mL portions of $CDCl_3$. The combined $CHCl_3$ layers were dried over $MgSO_4$. Concentration by rotoevaporation and high vacuum to remove residual solvent yielded 0.019 g (19% recovery) of a 1.7:1 mixture (by ^{31}P NMR) of **50** and **51** as a white solid: ^{31}P NMR ($CDCl_3$) δ +64.3, +66.5.

***anti*-9-Phenyl-9-phosphabicyclo[4.2.1]nona-2,4,6-triene (52).** To a solution of 0.4 g (1.8 mmol) of **23**[24] dissolved in 25 mL of benzene was added 1.0 mL of $HSiCl_3$ dropwise over several minutes. The solution was stirred at room temperature for 20 h before hydrolysis with 30% NaOH. The layers were separated, and the aqueous layer was extracted with two 20-mL portions of benzene. The combined benzene layers were dried over $MgSO_4$ and concentrated in vacuo to yield 0.1 g (30%) of phosphine **52** as a white solid: ^{31}P NMR ($CDCl_3$) δ −12.6 (lit.[70] δ −14).

Trichlorosilane Reduction of *trans*-2,2,3-Trimethyl-1-phenylphosphetane 1-Oxide. With Pyridine. To 1.5 mL (0.0144 mol) of trichlorosilane in 25 mL of dry benzene at 0 °C was slowly added a mixture of 1.5 mL (0.015 mol) of dry pyridine and 25 mL of dry benzene. To this mixture was added dropwise 1.0 g (0.0050 mol) of *trans*-2,2,3-trimethyl-1-phenylphosphetane 1-oxide in 25 mL of dry benzene. The solution was refluxed for 1 h under a nitrogen atmosphere and subsequently cooled in an ice bath while 80 mL of 30% sodium hydroxide was slowly added. The organic layer was separated and dried over magnesium sulfate. The solvent was removed, leaving a clear oil: ^{31}P NMR ($CDCl_3$) δ +25.3 (lit.[32] δ +27.9); ^{13}C NMR ($CDCl_3$) δ 16.8 (J_{PC} = 2.0, *C*H$_3$C-3), 19.4 (J_{PC} = 2.9, C-4), 22.6 (J_{PC} = 29.3, *trans*-*C*H$_3$C-2), 25.4 (*cis*-*C*H$_3$C-2), 36.8 (J_{PC} = 7.8, C-1), 43.1 (J_{PC} = 2.9, C-3), 127.5 (phenyl para C), 128.0 (J_{PC} = 4.9, phenyl meta C), 137.8 (J_{PC} = 32.2, phenyl ipso C), 131.6 (*J* = 15.6, phenyl ortho C).

Without Pyridine. To 1.0 g (0.0050 mol) of the phosphetane oxide in 40 mL of dry benzene was added 1.5 mL (0.015 mol) of trichlorosilane in 10 mL of dry benzene. The solution was refluxed for 1 h under a nitrogen atmosphere. With cooling in an ice bath, 80 mL of 30% sodium hydroxide was added to quench the reaction. The organic layer was separated and dried over magnesium sulfate. The solvent was removed leaving a clear oil: ^{31}P NMR ($CDCl_3$) δ +25.3 (trans isomer, 58.1%), +1.7 (cis isomer, 41.9%) (lit.[32] +27.9 and +3.3, respectively); ^{13}C NMR ($CDCl_3$) δ 16.0 (J_{PC} = 13.7, CH_3C-3), 22.4 (*cis*-*C*H$_3$C-2), 29.8 (J_{PC} = 24.4, *trans*-*C*H$_3$C-2), 39.1 (J_{PC} = 3.9, C-3), 127.3 (phenyl para C), 128.1 (J_{PC} = 2.9, phenyl meta C), 130.3 (J_{PC} = 14.6, phenyl ortho C), 139.8 (J_{PC} = 34.2, phenyl ipso C); C-2 and C-4 not clearly observed.

***exo*- (53) and *endo*-4-Methyl-4-Phosphatetracyclo[3.3.0^{2,8}.0^{3,6}]octane (3).** To 0.5 mL (50 mmol) of trichlorosilane in 20 mL of dry benzene was added 2 mL (25 mmol) of dry pyridine in 10 mL of dry benzene and 0.164 g (0.9 mmol) of oxide **2**. The mixture was refluxed 1 h. With cooling in an ice bath, 40 mL of 30% sodium hydroxide was added slowly. The organic layer was separated and dried over magnesium sulfate. The solvent was removed leaving a clear oil: ^{31}P NMR ($CDCl_3$) δ 47.4 (**53**, 67%) and +39.5 (**3**, 33%); lit.[14] +47.5 and +39.7, respectively.

(70) Katz, T. J.; Nicholson, C. R.; Reilly, C. A. *J. Am. Chem. Soc.* **1966**, *88*, 3832.