Cumulated Trienephosphine Oxides. Bimolecular Trapping of an Alkylidenecyclopropylidene[†]

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Dihalocarbene addition to allenic phosphine oxides occurs mainly at the allylic double bond. Treatment of dibromocarbene adducts with BuLi leads to cumulated trienephosphine oxides. In some cases, the intermediate alkylidenecyclopropylidene (or its precursor) is exceptionally stabilized, and this carbene (or carbenoid) is trapped by the corresponding cumulated trienephosphine oxide in a bimolecular process. The resultant spiropentane is formed in a regio- and stereoselective manner.

Introduction

A large class of thermally unstable substances consists of the α-haloorganolithium compounds.[3] These carbenoid compounds are exceptional because they react not only with electrophiles as is usual for "anions" but also with nucleophiles such as RLi[4] and also eliminate LiX with the formation of carbenes.

The electrophilic nature of carbenoids is perhaps their most intriguing property. Seebach and co-workers have shown that the carbenic character can be recognized by the strong downfield shift in the ^{13}C NMR signal of the α-carbon atom[5] (this is similar to that observed in carbocations).

The reactivity and stereochemistry observed in the reaction of these carbenoids has been interpreted by Walborsky as being due to metal-assisted ionization (MAI).[6] Carbenoids react with alkyllithium to give substitution products with inversion of configuration. These results suggest that the halide is the leaving group and not the lithium, thus leading to development of positive charge on carbon and can be explained by the reduction in the nucleophilicity of the carbanion with substitution of α-chloro groups.

Reaction between CCl_3Li and an olefin without intermediate carbene formation was first indicated by the high yields of 7,7-dichloronorcarane obtained by adding cyclohexene to $CBrCCl_3$ and MeLi at −100 °C.[7] The slow decomposition of (trichloromethyl)lithium in THF at −72 °C is accelerated by cyclohexene and other olefins.[8] A relatively rapid equilibrium is probably established between CCl_3Li and dichlorocarbene at −70 °C, from which the dichlorocarbene is removed by the alkene in a rate-determining process.[9]

gem-Lithiohalogenocyclopropanes, which are stable at temperatures around −100 °C, are important intermediates in organic synthesis. They can generally and conveniently be obtained through halogen−lithium exchange in reactions of the dihalogenocyclopropanes with alkyllithium.[10] These metalated species are easily trapped with electrophiles. At temperatures above −100 °C, the lithiohalocyclopropanes are converted to singlet cyclopropylidenes by formal loss of lithium halide.

Occasionally the cyclopropylidene to allene isomerization is disfavored for structural reasons; the reaction is then forced to follow an alternative path.[11,12] Despite a number of investigations, the precise reaction mechanism of the 1-halogeno-1-lithiocyclopropane opening to give allene is not fully clear, and the formation of free cyclopropylidene is questionable.[13] The most recent calculations indicate that the ring opening of cyclopropylidene proceeds via disrotation until the C_s transition state is reached at a C(1)−C(2)−C(3) angle of about 84.5°; disrotation continues with maintenance of C_s symmetry until a C(1)−C(2)−C(3) angle of about 100° is reached, at which point the reaction surface bifurcates into enantiomers via admixture of a conrotatory component, ultimately leading to allene.[14] The cyclopropylidene to

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(3) (a) Köbrich, G. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 41−52. (b) Köbrich, G. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 473−485.
(4) Topolski, M.; Duraisamy, M.; Rachon, J.; Gawronski, J.; Gawronska, K.; Goedken, V.; Walborsky, H. M. *J. Org. Chem.* **1993**, *58*, 546−555.
(5) (a) Seebach, D.; Siegel, H.; Müllen, K.; Hiltbrunner, K. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 784−785. (b) Siegel, H.; Hiltbrunner, K.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 785−786. (c) Seebach, D.; Siegel, H.; Gabriel, J.; Hässig, R. *Helv. Chim. Acta* **1980**, *63*, 2046−2053. (d) Seebach, D.; Hässig, R.; Gabriel, J. *Helv. Chim. Acta* **1983**, *66*, 308−337.
(6) Duraisamy, M.; Walborsky, H. M. *J. Am. Chem. Soc.* **1984**, *106*, 5035−5037.
(7) Miller, W. T., Jr.; Whalen, D. M. *J. Am. Chem. Soc.* **1964**, *86*, 2089−2090.

(8) (a) Hoeg, D. F.; Lusk, D. I.; Crumbliss, A. L. *J. Am. Chem. Soc.* **1965**, *87*, 4147−4155. (b) Köbrich, G.; Flory, K.; Merkle, H. R. *Tetrahedron Lett.* **1965**, 973−978.
(9) Köbrich, G.; Büttner, H.; Wagner, E. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 169−170.
(10) For reviews on the use of *gem*-dihalocyclopropanes in organic synthesis, see: (a) Backes, J.; Brinker, U. H. In *Methoden der Organischen Chemie (Houben-Weyl)*; Regitz, M., Ed.; Thieme Verlag: Stuttgart, 1989; Vol. E19b. (b) Kostikov, R. R.; Molchanov, A. P.; Hopf, H. *Top. Curr. Chem.* **1990**, *155*, 41−80. (c) Banwell, M. G.; Reum, M. E. *Adv. Strain Org. Chem.* **1991**, *1*, 19−64.
(11) (a) Skattebøl, L. *Tetrahedron Lett.* **1970**, 2361−2364. (b) Moore, W. R.; Taylor, K. G.; Müller, P.; Hall, S. S.; Gaibel, Z. L. F. *Tetrahedron Lett.* **1970**, 2365−2368. (c) Moore, W. R.; Hill, J. B. *Tetrahedron Lett.* **1970**, 4343−4346. (d) Moore, W. R.; Hill, J. B. *Tetrahedron Lett.* **1970**, 4553−4556.
(12) (a) Moore, W. R.; Ward, H. R. *J. Org. Chem.* **1960**, *25*, 2073. (b) Moore, W. R.; Ward, H. R.; Merritt, R. F. *J. Am. Chem. Soc.* **1961**, *83*, 2019−2020. (c) Marquis, E. T.; Gardner, P. D. *Tetrahedron Lett.* **1966**, 2793−2798. (d) Jones, M., Jr.; Petrillo, E. W., Jr. *Tetrahedron Lett.* **1969**, 3953−3956.
(13) Warner, P.; Sutherland, R. *J. Org. Chem.* **1992**, *57*, 6294−6300 and references therein.

allene transition state is electron deficient and resembles that for the cyclopropyl to allyl cation.
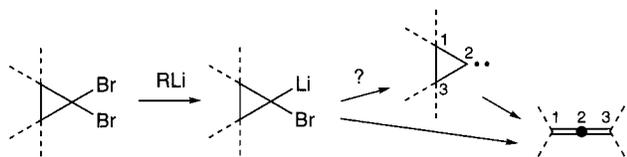
Cyclopropylidenes are transient metastable species and the parent has not yet been isolated experimentally. The energy barriers calculated[15] for its conversion to allene lie between 18 and 40 kcal mol^{-1} and are somewhat at variance with the experimental observations. Thus cyclopropylidene, generated by photolysis of matrix-isolated cyclopropylideneketene, gives ground-state propadiene at temperatures as low as 15 K.[16]

With the aim of preparing "push–pull" substituted cumulated trienes,[17] we have studied the addition of dihalocarbenes to allenic phosphine oxides followed by reaction of the products with BuLi.[18] Allenic phosphine oxides **3** are easily prepared by the method of Boisselle[19] (reaction of propargylic alcohols **1** with diarylphosphine chlorides **2**).[20,21]

Results

In general, the addition to the allenes **3** of dibromocarbene, dichlorocarbene,[22] or bromofluorocarbene,[23] generated by phase transfer catalysis, leads to alkylidene(dihalocyclopropyl)phosphine oxides **4** (Scheme 1).

For **3aα–3dα**, the addition of the dihalocarbene occurs on the double bond remote from the phosphine oxide

(14) The ring opening of diphenylcyclopropylidene gave rise to optically active 1,3-diphenylallene, but it was further pointed out that the cause for the retention of dissymmetry is dominated and probably limited to a steric effect, see: Jones, W. N.; Krause, D. L. *J. Am. Chem. Soc.* **1971**, *93*, 551–553.

(15) This isomerization of singlet cyclopropylidene to allene has been the subject of several theoretical investigations: method, activation energy (kcal mol^{-1}), exoergicity (kcal mol^{-1}), respectively. (a) MINDO/2, 13.7, 40: Bodor, N.; Dewar, M. J. S.; Maksic, Z. B. *J. Am. Chem. Soc.* **1973**, *95*, 5245–5249. (b) Simplex-INDO, 72, 25: Dillon, P. W.; Underwood, G. R. *J. Am. Chem. Soc.* **1977**, *99*, 2435–2446. (c) 4-31G, 18.2, 74.2: Pasto, D. J.; Haley, M.; Chipman, D. M. *J. Am. Chem. Soc.* **1978**, *100*, 5272–5278. (d) 4-31G, 11, 62.6: Honjou, N.; Pacansky, J.; Yoshimine, M. *J. Am. Chem. Soc.* **1984**, *106*, 5361–5363; **1985**, *107*, 5332–5341. (e) MP3/6-31G**, 11.5, 64.6: Rauk, A.; Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1985**, *107*, 3780–3786. (f) STO-3G, 14, 65: Valtazanos, P.; Elbert, S. T.; Ruedenberg, K. *J. Am. Chem. Soc.* **1986**, *108*, 3147–3149. (g) FORS, 14, 65: Valtazanos, P.; Elbert, S. T.; Xantheas, S.; Ruedenberg, K. *Theor. Chim. Acta* **1991**, *78*, 287–326. See also: Valtazanos, P.; Ruedenberg, K. *Theor. Chim. Acta* **1991**, *78*, 397–416.

(16) Monnier, M.; Allouche, A.; Verlaque, P.; Aycard, J. P. *J. Phys. Chem.* **1995**, *99*, 5977–5985.

(17) (a) For synthesis of donor–acceptor allenes, see: Saalfrank, R. W. *Isr. J. Chem.* **1985**, *26*, 181–190. (b) For preparation of cumulative hosts, see: Weber, E.; Seichter, W.; Wang, R.-J.; Mak, T. C. W. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 659–667.

(18) Santelli-Rouvier, C.; Santelli, M. *Tetrahedron Lett.* **1992**, *33*, 7843–7844.

(19) (a) Boisselle, A. P.; Meinhardt, N. A. *J. Org. Chem.* **1962**, *27*, 1828–1833. (b) Khusainova, N. G.; Pudovik, A. N. *Russ. Chem. Rev.* **1987**, *56*, 564–578.

(20) Clayden, J.; Warren, S. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 241–270.

(21) The anions of allenic phosphine oxide are known precursors for cumulatrienes; see: (a) Cadiot, P.; Chodkiewicz, W.; Borecka, B.; Charrier, C.; Simonnin, M.-P. *Chem. Abstr.* **1967**, *67*, 116923r. (b) Macomber, R. S.; Hemling, T. C. *Isr. J. Chem.* **1985**, *26*, 136–139. (c) Saito, I.; Yamaguchi, K.; Nagata, R.; Murahashi, E. *Tetrahedron Lett.* **1990**, *31*, 7469–7472.

(22) Weber, W. P.; Gokel, G. W. *Phase Transfer Catalysis in Organic Synthesis*; Springer-Verlag: New York, 1977; pp 18–43 and 58–62.

(23) Weyerstahl, P.; Blume, G.; Müller, C. *Tetrahedron Lett.* **1971**, 3869–3872.

Scheme 1

1a, R^1 = H, R^2 = R^3 = Me
1b, R^1 = R^2 = R^3 = Me
1c, R^1 = R^2 = Me, R^3 = *cyclo*-Pr
1d, R^1 = Me, R^2 = R^3 = *cyclo*-Pr
1e, R^1 = H, R^2 = R^3 = Ph
1f, R^1 = Ph, R^2 = R^3 = Me

2α, R = H
2β, R = Cl
2γ, R = Br
2δ, R = *t*-Bu

3aα, R = R^1 = H, R^2 = R^3 = Me
3bα, R = H, R^1 = R^2 = R^3 = Me
3bβ, R = Cl, R^1 = R^2 = R^3 = Me
3bγ, R = Br, R^1 = R^2 = R^3 = Me
3bδ, R = *t*-Bu, R^1 = R^2 = R^3 = Me
3cα, R = H, R^1 = R^2 = Me, R^3 = *cyclo*-Pr
3dα, R = H, R^1 = Me, R^2 = R^3 = *cyclo*-Pr
3eα, R = R^1 = H, R^2 = R^3 = Ph
3fα, R = H, R^1 = Ph, R^2 = R^3 = Me

**4aα, 4bα, 4bβ, 4bγ, 4bδ,
4cα, 4dα, X = Br**
5aα, X = F, X = Br
6bα, X = Cl

4eα

7aα
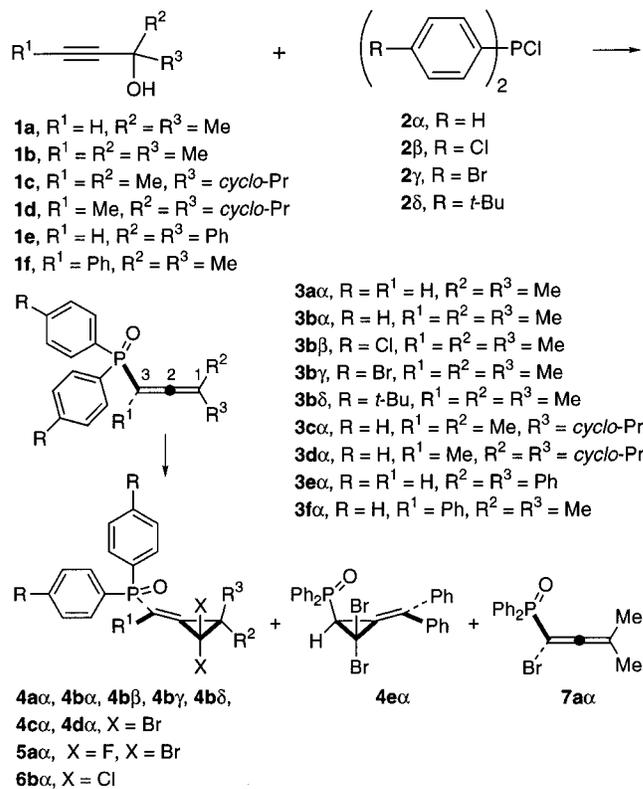
group (allylic position) to give **4**, **5aα**, and **6bα** (isolated product, 46–56% yield). This regioselectivity is independent of the nature of X. The configurations were assigned on the basis of the $^3J_{C–P}$ coupling constants. The only stereoisomer formed has the CX$_2$ group trans to the Ph$_2$PO one; this is shown by the fact that $J_{PC(X2)}$ is larger than $J_{PC(R^2R^3)}$ [$J_{PC(X2)}$ = 22–24 Hz; $J_{PC(R^2R^3)}$ = 6–10 Hz].[24]

With **3fα**, no addition occurred at all, the allene being recovered unchanged. In contrast, with **3eα**, addition of the dihalocarbene occurred at the double bond adjacent to the phosphine oxide forming **4eα**. Attempted addition of difluorocarbene (generated by phase transfer catalysis from dibromomethane and dibromodifluoromethane)[25] to **3aα** gave rise to a very unusual reaction with the isolation of bromoallene **7aα**.[26] Formally this arises from bromination of the carbanion generated by removal of the proton α to the phosphine oxide group.

Each of the dibromocyclopropanes **4aα–4dα** was treated with BuLi (THF, −90 to 0 °C). For **4aα**, the reaction gave rise to the enyne **8** (35% yield), resulting from α-lithiation followed by opening of the cyclopropane as shown.

4aα
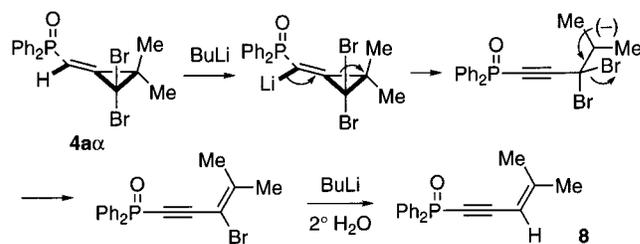
Compounds **4cα** and **4dα** gave the cumulated triene-phosphine oxides **10a** and **10b**, respectively, in moderate

(24) Albright, T. A.; Freeman, W. J.; Schweizer, E. E. *J. Am. Chem. Soc.* **1975**, *97*, 2946–2950.

(25) Balcerzak, P.; Fedorynski, M.; Jonczyk, A. *J. Chem. Soc., Chem. Commun.* **1991**, 826–827.

Scheme 2

a, R[2] = Me, R[3] = *cyclo*-Pr
b, R[2] = R[3] = *cyclo*-Pr

Scheme 3

α, R = H; β, R = Cl; γ, R = Br; δ, R = *t*-Bu

Figure 1. ORTEP plot of **14**δ.
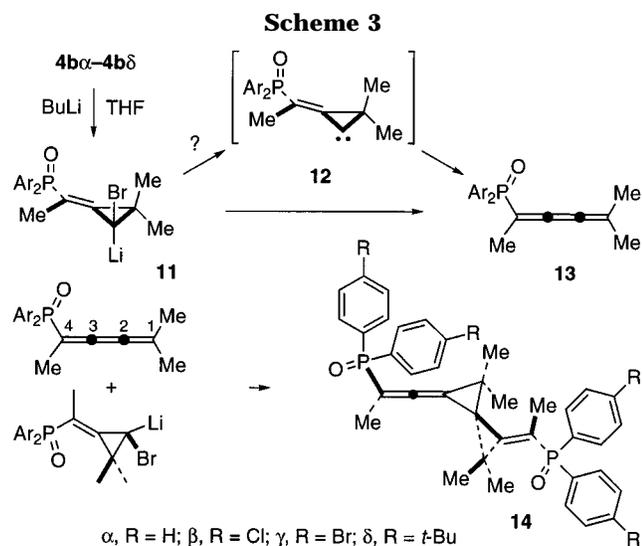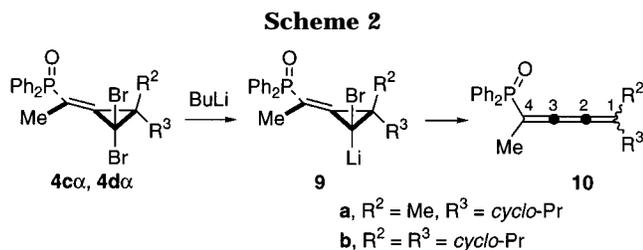
yield (40−45%);[27] **10a** was produced as a mixture of isomers (Scheme 2).[28]

In contrast, a spectacular result is observed with **4b**α−**b**δ. The only products are the spiropentanes **14**α−δ, each isolated as a single stereoisomer (Scheme 3). The formation of **14** must result from the bimolecular addition of the intermediate alkylidenecyclopropylidene **12** (or its corresponding carbenoid **11**) to the γ,δ-double bond of the trienic phosphine oxide **13**.

The stereochemistry of **14**δ (Figure 1) was determined by X-ray analysis and showed that if the allenic moiety has the configuration S*, the spiro carbon atom has the same configuration; further, the ethylenic double bond has the *E* geometry. The two diphenylphosphine oxide groups are present in a transoid orientation.[29]

Discussion

Regioselectivity of the Dihalocarbene Addition to Allenic Phosphine Oxides. Dibromo- and dichlorocarbene have been found to behave as electrophiles toward simple alkenes, reacting most rapidly with the

most highly alkylated olefins.[30] Steric effects in their cycloaddition with olefins are known to be small. Nevertheless, rate-retarding effects have been observed with double bonds which are substituted by bulky groups.[31] Consequently, the lack of reactivity of **3f**α may reasonably be attributed to steric hindrance. According to FMO theory, the favored approach of a carbene to an alkene is determined primarily by the interaction of the empty 2p orbital of the carbene with the olefinic π orbital. In line with their observed electrophilic character, calculations show that attack of the carbene should occur preferentially at the atom with the larger coefficient in the olefinic π orbital.[32] Previous results have shown that dibromocarbene adds to allenes exclusively at the more substituted double bond.[33] In this study, with the exception of **3e**α, addition occurred on the C(1)−C(2) double bond, which might be expected to be the more electron rich. Table 1 presents HOMO coefficients and energies of these allenic phosphine oxides as obtained by semiempirical calculations (AM1[34] and PM3[35] methods). We note that for **3e**α, which reacted at the C(2)−C(3) double bond, AM1 and PM3 results indicate, as expected, a larger coefficient on C(1) than on C(3). It appears, therefore, that the steric effect outweighs the electronic difference. For the allenic phosphine oxides **3b**α and **3d**α, the calculations confirmed the larger coefficient of the C(1)−C(2) double bond, and this is combined with a low polarization (HOMO, coeff. C(1)/coeff. C(2) = 0.96−1.22).[36] Further, the calculations show that C(3) bears a significant negative charge and hence would indicate

(26) (a) Berlan, J.; Capmau, M.-L.; Chodkiewicz, W. *C. R. Séances Acad. Sci.* **1971**, *273*, 1107−1110. (b) Berlan, J.; Capmau, M.-L.; Chodkiewicz, W. *Bull. Soc. Chim. Fr.* **1975**, 2259−2265.

(27) Concerning the addition of dihalocarbenes to allenes and conversion of the resulting methylenedihalocyclopropanes into trienic cumulenes, see: (a) Skattebol, L. *Tetrahedron Lett.* **1963**, 2175−2179. (b) Ball, W. J.; Landor, S. R.; Punja, N. *J. Chem. Soc. C* **1967**, 194−197. (c) Dewar, M. J. S.; Fonken, G. J.; Kirschner, S.; Minter, S. E. *J. Am. Chem. Soc.* **1975**, *97*, 6750−6753. (d) Bee, L. K.; Beeby, J.; Everett, J. W.; Garratt, P. J. *J. Org. Chem.* **1975**, *40*, 2212−2214. (e) Yakushkina, N. I.; Bolesov, I. G. *Zh. Org. Khim.* **1979**, *15*, 311−314. For the synthesis of strained cyclic cumulated trienes, see: (f) Moore, W. R.; Ozretich, T. M. *Tetrahedron Lett.* **1967**, 3205−3207. (g) Angus, R. O., Jr.; Johnson, R. P. *J. Org. Chem.* **1984**, *49*, 2880−2883. For a review, see: Johnson, R. P. *Chem. Rev. (Washington, D.C.)* **1989**, *89*, 1111−1124.

(28) Roth, W. R.; Exner, H.-D. *Chem. Ber.* **1976**, *109*, 1158−1162.

(29) Optimized PM3 calculations give bond lengths and angles which are close to the experimental values, the main discrepancies concerning the C−P bond lengths.

(30) (a) Moss, R. A. *Acc. Chem. Res.* **1980**, *13*, 58−64. (b) Rondan, N. G.; Houk, K. N.; Moss, R. A. *J. Am. Chem. Soc.* **1980**, *102*, 1770−1776.

(31) Giese, B.; Lee, W. B.; Stiehl, C. *Tetrahedron Lett.* **1983**, *24*, 881−884.

(32) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley: London, 1976.

(33) (a) Ball, W. J.; Landor, S. R. *Proc. Chem. Soc.* **1961**, 246. (b) Bézaguet, A. *C. R. Acad. Sci., Paris* **1962**, *257*, 3371−3373. (c) Rahman, W.; Kuivila, H. G. *J. Org. Chem.* **1966**, *31*, 772−776. (d) Landor, S. R. *The Chemistry of the Allenes*; Academic Press: London, 1982; Vol. 2, pp 351−360. (e) Schuster, H. E.; Coppola, G. M. *Allenes in Organic Synthesis*; Wiley-Interscience: New York, 1984.

(34) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Steward, J. P. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902−3909.

(35) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209−220 and 221−264.

(36) For comprehensive discussions concerning the effects of orbital polarization in the carbene addition to olefins, see: Fox, D. P.; Stang, P. J.; Apeloig, Y.; Karni, M. *J. Am. Chem. Soc.* **1986**, *108*, 750−756.

Table 1. FMO Energies, Coefficients, and Optimized Bond Lengths[a] of Cumulated Diene- and Trienephosphine Oxides

	allenic phosphine oxides[b]	cumulated trienes[c]	cumulated trienephosphine oxides[e]
energy	ΔH_f (kcal/mol), **3b**α: 29.0;[f] 3.6[g] **3d**α: 85.5;[f] 63.9[g] **3e**α: 102.0;[f] 73.6[g]	energy (au), **20a**: $-154.21067^{d,h}$ **20b**: -232.58480;[d] ZPE (kcal/mol): 70.6;[d,i] -229.29887^{j}	ΔH_f (kcal/mol), **10b**: 116.3;[f] 92.1[g] **13**α: 59.7;[f] 32.3;[g] -711262.26^{j}
HOMO, eV	**3b**α: -9.157;[f] -9.659^{g} **3d**α: -9.180;[f] -9.545^{g} **3e**α: -8.845;[f] -9.016^{g}	**20a**: -9.007^{d} **20b**: -8.363;[d] -6.738^{j}	**10b**: -8.866;[f] -9.076^{g} **13**α: -8.801;[f] -9.152;[g] -5.776^{j}
LUMO, eV	**3b**α: 0.069;[f] -0.174^{g} **3d**α: 0.036;[f] -0.188^{g} **3e**α: -0.309;[f] -0.438^{g}	**20a**: 2.578^{d} **20b**: 2.933;[d] 5.931^{j}	**10b**: -0.572;[f] -0.912^{g} **13**α: -0.532;[f] -0.854;[g] 5.477^{j}
HOMO coeff	**3b**α: $C(1) = -0.44$; $C(2) = -0.36$; $C(3) = 0.32^{f}$ **3d**α: $C(1) = -0.50$; $C(2) = -0.44$; $C(3) = 0.33^{f}$ **3e**α: $C(1) = -0.36$; $C(2) = -0.36$; $C(3) = 0.25^{f}$	**20a**: $C(1) = -C(4) = 0.55$; $C(2) = -C(3) = 0.39^{d}$ **20b**: $C(1) = -0.56$; $C(2) = -0.48$; $C(3) = 0.37$; $C(4) = 0.59^{d}$	**10b**: $C(1) = -0.50$; $C(2) = -0.39$; $C(3) = 0.34$; $C(4) = 0.53^{f}$ **10b**: $C(1) = -0.44$; $C(2) = -0.41$; $C(3) = 0.27$; $C(4) = 0.52^{g}$ **13**α: $C(1) = -0.44$; $C(2) = -0.35$; $C(3) = 0.29$; $C(4) = 0.46^{f}$ **13**α: $C(1) = -0.41$; $C(2) = -0.36$; $C(3) = 0.26$; $C(4) = 0.47^{g}$
LUMO coeff	**3b**α: $C(1) = 0.07$; $C(2) = -0.04$; $C(3) = -0.07^{f}$ **3d**α: $C(1) = 0.08$; $C(2) = -0.07$; $C(3) = -0.06^{f}$ **3e**α: $C(1) = 0.28$; $C(2) = -0.37$; $C(3) = -0.05^{f}$	**20a**: $C(1) = C(4) = -0.67$; $C(2) = C(3) = 0.46^{d}$ **20b**: $C(1) = -0.78$; $C(2) = 0.48$; $C(3) = 0.79$; $C(4) = -0.76^{d}$	**10b**: $C(1) = -0.56$; $C(2) = 0.35$; $C(3) = 0.39$; $C(4) = -0.52^{f}$ **10b**: $C(1) = 0.56$; $C(2) = -0.32$; $C(3) = -0.42$; $C(4) = 0.49^{g}$ **13**α: $C(1) = -0.49$; $C(2) = 0.30$; $C(3) = 0.34$; $C(4) = -0.46^{f}$ **13**α: $C(1) = 0.50$; $C(2) = -0.28$; $C(3) = -0.37$; $C(4) = 0.43^{g}$
net charges	**3b**α: $C(1) = -0.078$; $C(2) = -0.139$; $C(3) = -0.429^{f}$ **3d**α: $C(1) = -0.020$; $C(2) = -0.124$; $C(3) = -0.428^{f}$ **3e**α: $C(1) = -0.012$; $C(2) = -0.071$; $C(3) = -0.481^{f}$	**20a**: $C(1) = C(4) = -0.38$; $C(2) = C(3) = 0.07^{d}$ **20b**: $C(1) = -0.11$; $C(2)\ 0.08$; $C(3) = 0.03$; $C(4) = -0.40^{d}$	**10b**: $C(1) = 0.075$; $C(2) = -0.178$; $C(3) = -0.037$; $C(4) = -0.431^{f}$ **10b**: $C(1) = 0.108$; $C(2) = -0.197$; $C(3) = -0.029$; $C(4) = -0.793^{g}$ **13**α: $C(1) = 0.026$; $C(2) = -0.195$; $C(3) = -0.031$; $C(4) = -0.439^{f}$ **13**α: $C(1) = 0.044$; $C(2) = -0.196$; $C(3) = 0.027$; $C(4) = -0.791^{g}$
distances C(1)−C(2)	**3b**α: 1.310;[f] 1.309[g] **3d**α: 1.312;[f] 1.313[g] **3e**α: 1.317;[f] 1.318[g]	**20a**: 1.302^{d} **20b**: 1.307;[d] 1.301^{j}	**10b**: 1.316;[f] 1.318[g] **13**α: 1.315;[f] 1.315;[g] 1.302^{j}
C(2)−C(3)	**3b**α: 1.300;[f] 1.302[g] **3d**α: 1.300;[f] 1.302[g] **3e**α: 1.292;[f] 1.293[g]	**20a**: 1.264^{d} **20b**: 1.264;[d] 1.254^{j}	**10b**: 1.264;[f] 1.260[g] **13**α: 1.263;[f] 1.260;[g] 1.255^{j}
C(3)−C(4)		**20b**: 1.304;[d] 1.297^{j}	**10b**: 1.308;[f] 1.309[g] **13**α: 1.308;[f] 1.309;[g] 1.297^{j}

[a] Bond lengths are expressed in angstroms. [b] Atom numbering is as in Scheme 1. [c] Atom numbering is as in Scheme 4. [d] 6-31G** level, estimation of the correlation energy changes by Møller−Plesset perturbation theory truncated to second order (MP2). [e] Atom numbering is as in Schemes 2 and 3. [f] Semiempirical PM3 study. [g] Semiempirical AM1 study. [h] See ref 37. [i] Zero-point energies (ZPEs) are scaled by 0.90, see ref 47. [j] MP2/STO-3G level.

that the regioselectivity of the dihalocarbene addition does not involve a charge effect. In other words, the attack of the alkene on the carbene is controlled by FMO factors and not by Coulombic ones. Finally, we propose that the high facial selectivity observed arises from steric repulsion between the bulky diphenylphosphine oxide group and the carbenic carbon atom.

Formation of Adducts 14 and the Stereoselectivity in Addition. The reaction of alkylidenedibromocyclopropanes with alkyllithiums is known to lead to the corresponding cumulated trienes, and this observation was confirmed by the formation of **10a** and **10b**.[27,38] The dramatic change observed in the case of **4b**α−δ was unexpected and striking. In examining reasons for this result we considered that they may, at least in principle, be found in the greater stabilility of the carbenoid **11** (or the alkylidenecyclopropylidene **12**) and also be associated

with a greater reactivity of the C(1)−C(2) double bond of the triene **13**. Despite the fact that detailed ab initio analyses for the energy surface of the ring opening of cyclopropylidene to allene are in good agreement with other reliable theoretical data, it remains true that calculations have not so far reproduced the experimental observations.[15g,39] The opening of **11** (or **12**) will be dependent on its geometry. Comparison shows that the lengths of the C−C bonds in the ring of methylenecyclopropane are significantly different from those of cyclopropane. In methylenecyclopropane **22**, the bond opposite the ethylenic carbon, i.e., the C(1)−C(2) bond is lengthened (1.541 Å)[40] relative to cyclopropane **21** itself (1.514 Å)[41] whereas the adjacent bond C(1)−C(3) is shortened (1.457 Å). This effect corresponds to a weakening of the former (by about 6−8 kcal/mol) and a strengthening of the latter bond. The optimized geom-

(37) Liang, C.; Allen, L. C. *J. Am. Chem. Soc.* **1991**, *113*, 1873−1878.

(38) Reactions of butatrienes with dichlorocarbene yield the monoaddition products on C(1)−C(2) double bond and pentatetraenes are formed with methyllithium: Karich, G.; Jochims, J. C. *Chem. Ber.* **1977**, *110*, 2680−2694. See also: Yakushkina, N. I.; Bolesov, I. G. *Zh. Org. Khim.* **1979**, *15*, 311−314.

(39) Calculations reveal a sudden change in energy and/or a geometric variable, corresponding to a small increase in the parameter in question ("catastrophic collapse"), see ref 15b.

(40) Laurie, V. W.; Stigliani, W. M. *J. Am. Chem. Soc.* **1970**, *92*, 1485−1488.

(41) Jones, W. J.; Stoicheff, B. P. *Can. J. Phys.* **1964**, *42*, 2259−2263.

Table 2. Optimized Energies and Bond Lengths and Angles[a] of Carbenoids 24a, 24b, and 11α Calculated Using the ab Initio Mp2/Sto-3G[b] and Comparison of Geometrical Data with 22 and 23[c]

	24a	24b	11α	22[d]	23[e]		24a	24b	11α	22	23
energy (au)	−2704.1079	−2782.25538	−3686.4349			angles					
LUMO (eV)	2.798	2.888	2.774			C(1)−C(2)−C(3)	58.8	59.0	59.2	58.1	57.7
HOMO (eV)	−6.695	−6.511	−5.612			C(2)−C(1)−C(3)	58.5	58.2	58.3		58.8
net charges						C(1)−C(3)−C(2)	62.7	62.8	62.5	63.5	63.6
C(1)	−0.157	0.002	0.004			Li−C(2)−C(1)	149.8	149.8	150.0		
C(2)	−0.039	−0.048	−0.050			Li−C(2)−C(3)	150.7	150.1	149.6		
C(3)	−0.022	−0.029	−0.042			α	175.3	174.0	173.8		
C(4)	−0.139	−0.143	−0.151			Br−C(2)−C(1)	113.0	115.8	115.9		
Br	−0.009	−0.005	−0.007			Br−C(2)−C(3)	112.5	113.7	113.8		
Li	0.095	0.080	0.086			β	116.4	118.8	118.9		
P			0.883			Br−C(2)−Li	68.2	67.1	67.3		
O			−0.522			C(1)−C(3)−C(4)	148.4	148.6	153.1	148.2	150.9
bond lengths						C(2)−C(3)−C(4)	148.8	148.5	144.4		145.5
C(1)−C(2)	1.533	1.538	1.534	1.541	1.545	C(3)−C(4)−C(7)			120.9		
C(2)−C(3)	1.470	1.470	1.471	1.457	1.458	C(3)−C(4)−P			126.8		
C(1)−C(3)	1.476	1.482	1.485		1.476	C(5)−C(1)−C(6)		112.9	112.7		
C(3)−C(4)	1.301	1.301	1.305	1.332	1.302	C(2)−C(3)−C(4)−H(7)	1.7	0.7			4.55
C(4)−P			1.840			C(2)−C(3)−C(4)−H(8)	−178.7	−179.9			
P−O			1.622			C(2)−C(3)−C(4)−C(7)			1.4		
C(2)−Li	1.899	1.895	1.892			C(2)−C(3)−C(4)−P			−175.9		
C(2)−Br	2.051	2.043	2.040			C(3)−C(4)−P−O			137.6		
Br−Li	2.217	2.180	2.182								

[a] Bond lengths and angles are expressed in angstroms and degrees, respectively. [b] STO-3G level, estimation of the correlation energy changes by Møller−Plesset perturbation theory truncated to second order (MP2). [c] Atom numbering is as in Scheme 4. [d] From rotational spectrum, see ref 40. [e] From X-ray crystallography, see ref 42.

Scheme 4

15	**16**	**17**	**18a**, R = H	**12α**, R = Me
			18b, R = Me	**19**, R = cyclo-Pr

20a, R = H	**21**	**22**	**23**
20b, R = Me			

24a	**24b**	**11α**	
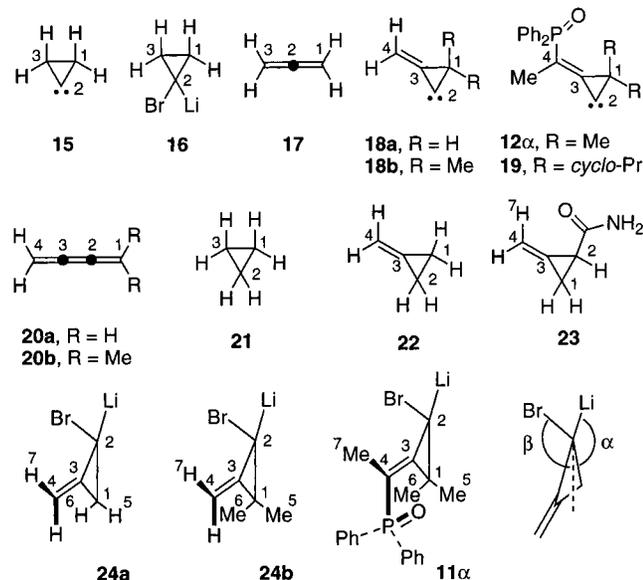
etries of carbenoids **11α**, **24a**, and **24b** (see Table 2 and Scheme 4) or alkylidenecyclopropylidenes **12α**, **18a**, and **18b** (see Table 3) are similar. The changes in molecular geometry, and hence bond energies, must exert a strong influence on the chemical behavior of the 1-alkylidene-2-bromo-2-lithiocyclopropanes or alkylidenecyclopropylidenes. In those reactions in which ring opening takes place, it is the C(1)−C(2) bond that should be broken preferentially and not the C(1)−C(3) bond.[42]

Structures and stabilities of some carbenoids have been calculated with 3-21G basis sets, and in particular, it appears that LiCH₂Cl has a bridged structure.[43] Calculations concerning the carbenoids **11α**, **24a**, and **24b**

(42) In addition, the C(1)−C(3)−C(4) and C(2)−C(3)−C(4) angles in the carbenes **18a**, **18b** or carbenoids **11α** are 152.7, 153.8, 153.1° and 143.0, 142.3, 144.4°, respectively. Thus the exocyclic carbon is displaced from the plane perpendicular to the ring and bissecting the C(1)−C(3)−C(2) angle so as to be closer to C(2). Similar molecular distortions were revealed in the structure determined by X-ray crystallography of methylenecyclopropane-2-carboxamide, see: Van Derveer, D. G.; Baldwin, J. E.; Parker, D. W. *J. Org. Chem.* **1987**, *52*, 1173−1174.

Table 3. Optimized Energies and Bond Lengths and Angles[a] of Cyclopropylidenes 15, 18a, 18b, and 12α Calculated Using the ab Initio RHF/MP2/6-31G or RHF/MP2/STO-3G[b]**

	15[c]	18a[c]	18b[c]	12α[d]
energy (au)	−116.15526	−154.11245	−232.48619	−1132.20660
ZPE (kcal/mol)	36.4[e]		69.9[f]	
LUMO (eV)	2.4766	1.2890	1.4538	4.5060
HOMO (eV)	−9.7056	−9.6041	−9.2019	−6.0218
net charges				
C(1)	−0.362	−0.383	−0.173	−0.046
C(2)	0.062	0.031	0.031	0.033
C(3)		−0.042	−0.032	−0.119
C(4)		−0.253	−0.271	−0.098
bond lengths				
C(1)−C(2)	1.495	1.535	1.531	1.553
C(2)−C(3)		1.438	1.446	1.480
C(1)−C(3)	1.478	1.445	1.448	1.467
C(3)−C(4)		1.317	1.317	1.312
C(1)−C(4)[g]		2.684	2.694	2.708
C(2)−C(4)[g]		2.613	2.615	2.646
angles				
C(1)−C(2)−C(3)	59.2	58.0	58.1	57.7
C(2)−C(1)−C(3)	60.4	57.6	58.0	58.7
C(1)−C(3)−C(2)		64.3	63.9	63.5
C(1)−C(3)−C(4)		152.7	153.8	154.0
C(2)−C(3)−C(4)		143.0	142.3	142.4

[a] Bond lengths and angles are expressed in angstroms and degrees, respectively. [b] Atom numbering is as in Scheme 4. [c] 6-31G** level, estimation of the correlation energy changes by Møller−Plesset perturbation theory truncated to second order (MP2). [d] MP2.STO-3G. [e] See ref 15e. [f] Zero-point energies (ZPEs) are scaled by 0.90, see ref 47. [g] Distance between nonbonded atoms.

(Table 2) reveal a rehybridization at the carbenoid carbon atom with an increase in the s character of the C−Li bond and in the p character of the C−Br bond (for **11α**, α = 173.8° and β = 118.9° instead of 123.2° in methylenecyclopropane).[5d,44,45] Furthermore, the C(2)−Br distance of 2.04 Å is distinctly elongated as anticipated and is about 0.13 Å longer than the C−Br bond in *gem*-dibromocyclopropanes.[46] Although the presence of the

(43) Schleyer, P. v. R.; Clark, T.; Kos, A. J.; Spitznagel, G. W.; Rohde, C.; Arad, D.; Houk, K. N.; Rondan, N. G. *J. Am. Chem. Soc.* **1984**, *106*, 6467−6475.

(44) In methylenecyclopropane, the value of the H−C−H (ring) angle is 113.5 ± 1°, see ref 40.

Table 4. Exoergicity of the Conversion of Cyclopropylidenes to Cumulenes

method	cyclopropylidene ΔH_f or energy (kcal/mol)	cumulene ΔH_f or energy (kcal/mol)	exoergicity (kcal/mol)
	15	**17**	
PM3	114.36	46.98	67.38
AM1	120.97	46.05	74.92
MP2/6-31G**	−72888.53	−72954.49	65.96[a]
	18a	**20a**	
PM3	141.45	78.54	62.91
AM1	148.81	75.99	72.82
MP2/6-31G**	−96707.04	−96768.67	61.63
	18b	**20b**	
PM3	128.83	59.69	69.14
AM1	138.32	59.13	79.19
MP2/6-31G**	−145887.31	−145949.19	61.88
	12α	**13α**	
PM3	131.70	59.76	71.94
AM1	118.65	32.29	86.36
MP2/STO−3G	−711188.87	−711262.32	73.45
	19	**10b**	
PM3	189.09	116.33	72.76
AM1	178.93	92.15	86.78

[a] See ref 15f.

Table 5. Calculated Energies for the Formation of Cyclopropylidenes and LiBr from Carbenoids at the MP2/STO-3G Level

carbenoid energy (kcal/mol)	cyclopropylidene energy (kcal/mol)	ΔE (kcal/mol)
16	**15**	
−1673374.43	−71847.80	57.44
24a	**18a**	
−1696853.56	−95326.74	57.63
24b	**18b**	
−1745342.68	−143814.87	58.62
11α	**12α**	
−2312716.15	−711188.87	58.09

diphenylphosphine oxide group does not modify the charges or the energy of the LUMO, it leads, significantly, to a higher level for the HOMO ($\Delta E \approx 0.9$ eV). The presence of the diphenylphosphine oxide group also increases the exoergicity of the conversion from alkylidenecyclopropylidene to butatriene (Table 4).

The formation of cyclopropylidenes by elimination of LiBr from the carbenoids is an endothermic process with an energy change in the range 57.4−58.6 kcal/mol at the MP2/STO-3G level (energy of LiBr: −1 601 469.19 kcal/mol) (Table 5).

In considering our proposal, that the reactivity of the trienes **13** may be enhanced, we have carried out ab initio and PM3 or AM1 molecular orbital calculations for butatriene, cumulated diene and trienephosphine oxides (Table 1). These reveal a relatively high HOMO energy and a particularly low LUMO energy for trienephosphine oxides **10b** and **13α** (Scheme 5). Thus the introduction of the diphenylphosphine oxide group causes a significant lowering of the LUMO energy level compared with the

(45) A rehybridization at the alkylidene carbenoid carbon atom was confirmed by X-ray crystallographic analysis of the 1-chloro-1-lithio-2,2-diphenylethene; see: Boche, G.; Marsch, M.; Müller, A.; Harms, K. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1032−1033. See also, Maercker, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1023−1025.

(46) It should be noted that ¹³C NMR evidence suggests a weak, highly polarized C−Br bond in cyclopropylcarbenoids; see ref 5. The carbon−bromine bond length value in *gem*-dibromocyclopropanes is 1.91 ± 0.01 Å. See: Paquette, L. A.; Fristad, W. E.; Schuman, C. A.; Beno, M. A.; Christoph, G. G. *J. Am. Chem. Soc.* **1979**, *101*, 4645−4655.

(47) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; John Wiley & Sons: New York, 1986; p 251.

Scheme 5

Scheme 6

corresponding cumulene ($\Delta E \approx 0.5$ eV). These effects are more important for **13α**. Recalling that the cycloadditions of carbenes (or carbenoids) to alkenes are LU(carbene)−HO(alkene) controlled (the "electrophilic term"),[32,48] we note that for the cumulated trienephosphine oxides and the phosphine oxide substituted carbenoids, the interaction LU(triene)−HO(carbenoid) (the "nucleophilic term") becomes an important contributor which can explain the increased rate of cycloaddition. Moreover, at the STO-3G level the HOMO of **13α** is essentially a C(2)−C(3) π-orbital interacting with the P=O group orbital (energy, −5.776 eV, coeff. (p_z) C(1), 0.02; C(2), −0.20; C(3), −0.11; C(4), 0.23; O, 0.782), the π-orbital of the 1,3-diene is the HOMO-2 (energy, −6.727 eV, coeff. (p_y) C(1), 0.430; C(2), 0.325; C(3), −0.295; C(4), −0.457). In contrast, the LUMO is the π^*-orbital of the 1,3-diene, as expected (energy, 5.477 eV, coeff. (p_y) C(1), −0.534; C(2), 0.330; C(3), 0.378; C(4), −0.516).

The conversion from carbenoid to carbene results in a decrease in the energy of the LUMO of **12α** relative to **11α**, consequently the interaction LU(carbene)−HO(triene) becomes more important as that between LU(triene) and HO(carbene). This would also favor an increase in the rate of addition of carbene.

In considering the stereoselectivity of the addition of **11** (or **12**) to **13**, it is obvious that it cannot be accounted for by an "open" transition state. Consequently, we favor the "compact" transition state depicted in Scheme 6 as the most probable. Such a transition state keeps the bulky diarylphosphinyl groups apart, while allowing

(48) Moss, R. A.; Perez, L. A.; Wlostowska, J.; Guo, W.; Krogh-Jespersen, K. *J. Org. Chem.* **1982**, *47*, 4177−4180.

nucleophilic attack of the anion onto the triene, followed by expulsion of the bromide, and also permitting favorable secondary FMO interactions. These secondary interactions are shown more clearly in the carbene– or carbenoid–triene pictures in Scheme 5.

This interaction of LU(triene) with HO(carbenoid) can be regarded as a nucleophilic addition of the carbanion part of **11** to **13** leading to a phosphorus-stabilized propargyl anion.[49] Such an interaction cannot occur in the addition of carbenoids to simple alkenes.

Conclusion

In conclusion, the formation of the spiro compounds **14** probably results from a combination of factors: (a) the slow rate of opening of the alkylidenecyclopropane compounds **11** (or **12**), (b) the presence of the diphenylphosphine oxide group which increases the energy of the HOMO of **11** (or **12**), (c) the presence of the diphenylphosphine oxide group which lowers the energy of the LUMO of **13**, and (d) the stereoselectivity of the addition being controlled by the stabilizing secondary orbital interactions in the transition state.

Experimental Section

General. All reactions were run under argon in oven-dried glassware. TLC was performed on silica gel 60 F$_{254}$. ^{1}H and ^{13}C NMR spectra were recorded in CDCl$_3$ solutions at 400, 200 and 100, 50 MHz, respectively. Diarylphosphine chlorides **2** were prepared according to the literature procedure.[50]

General Procedure for the Preparation of Allenic Phosphine Oxides. To a stirred and cooled (0 °C) solution of the acetylenic alcohol (20 mmol) in anhydrous ether (20 mL) and pyridine (1.94 mL, 24 mmol) under argon was added dropwise diarylphosphine chloride (20 mmol) in CH$_2$Cl$_2$ (20 mL). The stirring was maintained 1 h at 0 °C and at room temperature overnight. The solution was then poured onto ice and extracted with CH$_2$Cl$_2$, and the organic layer was dried (MgSO$_4$). Concentration in vacuo gave the crude product that was subjected to flash chromatography on silica gel eluting with ether.

3-Methyl-1-(diphenylphosphinyl)-1,2-butadiene (3aα). Reaction of **1a** and **2α** following the general procedure gave **3aα**: 75–80% yield; mp 71–72 °C;[19a,51] IR 1958, 1440 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.73–7.62 (m, 4H), 7.43 (m, 6H), 5.61 (sept., *J* = 3.2 Hz, 1H), 1.47 (dd *J* = 6.3, 3.2 Hz, 6H); ^{13}C NMR (CDCl$_3$) δ 208.6 (s), 133.1 (d, *J*$_{PC}$ = 105.0 Hz) (s), 131.8–131.0 (d), 128.5–128.1 (d), 97.6 (d, *J*$_{PC}$ = 13.0 Hz) (s), 83.7 (d, *J*$_{PC}$ = 107.0 Hz) (d), 18.8 (*J*$_{PC}$ = 5.5 Hz) (q); ^{31}P NMR (CDCl$_3$) δ 24.90.

4-Methyl-2-(diphenylphosphinyl)-2,3-pentadiene (3bα). Reaction of **1b** and **2α** following the general procedure gave **3bα**, 82% yield; mp 89–90 °C; IR 1953, 1438 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 8.00–7.33 (m, 10H), 1.91 (d, *J* = 12.0 Hz, 3H), 1.43 (d, *J* = 7.0 Hz, 6H); ^{13}C NMR (CDCl$_3$) δ 207.7 (d, *J*$_{PC}$ = 7.0 Hz) (s), 131.6 (d, *J*$_{PC}$ = 103.0 Hz) (s), 131.0–127.0 (d), 96.7 (d, *J*$_{PC}$ = 14.5 Hz) (s), 90.4 (d, *J*$_{PC}$ = 103.5 Hz) (s), 18.8 (d, *J*$_{PC}$ = 6.1 Hz) (q), 13.7 (d, *J*$_{PC}$ = 8.5 Hz) (q); ^{31}P NMR (CDCl$_3$) δ 32.0. Anal. Calcd for C$_{18}$H$_{19}$OP: C, 76.58; H, 6.78. Found: C, 76.48; H, 6.72.

4-Methyl-2-[bis(4-chlorophenyl)phosphinyl]-2,3-pentadiene (3bβ). Reaction of **1b** and **2β** following the general procedure gave **3bβ**: 66% yield; mp 104–106 °C; IR 1962 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.49–7.20 (m, 8H), 1.68 (d, *J* = 12.0 Hz, 3H), 1.25 (d, *J* = 6.4 Hz, 6H); ^{13}C NMR (CDCl$_3$) δ 208.8 (d, *J*$_{PC}$

= 7.2 Hz) (s), 132.6 (d, *J*$_{PC}$ = 10.4 Hz) (d), 128.4 (d, *J*$_{PC}$ = 12.6 Hz) (d), 128.2 (d, *J*$_{PC}$ = 3.3 Hz) (s), 97.4 (d, *J*$_{PC}$ = 14.5 Hz) (s), 90.2 (d, *J*$_{PC}$ = 105.7 Hz) (s), 19.1 (d, *J*$_{PC}$ = 5.9 Hz) (q), 13.9 (d, *J*$_{PC}$ = 8.7 Hz) (q); ^{31}P NMR (CDCl$_3$) δ 29.7; MS *m/z* 355 (18), 352 (44), 350 (66), 269 (100), 235 (17), 170 (13), 159 (21), 152 (14); HRMS calcd for C$_{18}$H$_{17}$OP^{35}Cl$_2$ 350.03940, found 350.0402.

4-Methyl-2-[bis(4-bromophenyl)phosphinyl]-2,3-pentadiene (3bγ). Reaction of **1b** and **2γ** following the general procedure gave **3bγ**: 72% yield; IR 1967 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.57–7.42 (m, 8H), 1.82 (d, *J* = 12.0 Hz, 3H), 1.39 (d, *J* = 6.5 Hz, 6H); ^{13}C NMR (CDCl$_3$) δ 208.3 (s), 132.9 (d, *J*$_{PC}$ = 10.0 Hz) (d), 131.6 (d, *J*$_{PC}$ = 12.0 Hz) (d), 130.9 (d, *J*$_{PC}$ = 105.0 Hz) (s), 97.6 (d, *J*$_{PC}$ = 14.6 Hz) (s), 90.3 (d, *J*$_{PC}$ = 105.0 Hz) (s), 19.3 (d, *J*$_{PC}$ = 5.8 Hz) (q), 14.1 (d, *J*$_{PC}$ = 8.1 Hz) (q). Anal. Calcd for C$_{18}$H$_{17}$Br$_2$OP: C, 49.12; H, 3.89. Found: C, 49.24; H, 3.92.

4-Methyl-2-[bis(4-*tert*-butylphenyl)phosphinyl]-2,3-pentadiene (3bδ). Reaction of **1b** and **2δ** following the general procedure gave **3bδ**: 68%; IR 1965 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.59–7.49 (m, 4m), 7.38–7.33 (m, 4H), 1.79 (d, *J*$_{PC}$ = 11.8 Hz, 3H), 1.29 (d, *J*$_{PC}$ = 6.4 Hz, 6H), 1.22 (s, 9H); ^{13}C NMR (CDCl$_3$) δ 207.9 (d, *J*$_{PC}$ = 6.8 Hz) (s), 154.7 (d, *J*$_{PC}$ = 2.8 Hz) (s), 131.3 (d, *J*$_{PC}$ = 9.8 Hz) (d), 128.8 (d, *J*$_{PC}$ = 106.0 Hz) (s), 125.1 (d, *J*$_{PC}$ = 12.0 Hz) (d), 96.7 (d, *J*$_{PC}$ = 14.2 Hz) (s), 91.0 (d, *J*$_{PC}$ = 103.0 Hz) (s), 34.8 (s), 31.0 (q), 19.2 (d, *J*$_{PC}$ = 6.2 Hz) (q), 14.0 (d, *J*$_{PC}$ = 8.1 Hz) (q). Anal. Calcd for C$_{26}$H$_{35}$OP: C, 79.15; H, 8.94. Found: C, 79.24; H, 8.89.

4-Cyclopropyl-2-(diphenylphosphinyl)-2,3-pentadiene (3cα). Reaction of **1c** and **2α** following the general procedure gave **3cα**: 67% yield; IR 1952, 1440 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.7 (m, 4H), 7.45 (m, 6H), 1.88 (d, *J* = 11.7 Hz, 3H), 1.45 (d, *J* = 6.2 Hz, 3H), 0.93 (m, 1H), 0.45 (m, 2H), 0.08 (m, 1H), −0.32 (m, 1H); ^{13}C NMR (CDCl$_3$) δ 207.1 (s), 131.0–129.0 (d), 103.7 (d, *J*$_{PC}$ = 14.0 Hz) (s), 93.0 (d, *J*$_{PC}$ = 103.7 Hz) (s), 16.7 (d, *J*$_{PC}$ = 5.9 Hz) (d or q), 14.3 (d, *J*$_{PC}$ = 8.3 Hz) (d or q), 12.8 (d, *J*$_{PC}$ = 6.5 Hz) (d or q), 5.2 (t); ^{31}P NMR (CDCl$_3$) δ 30.8. Anal. Calcd for C$_{20}$H$_{21}$OP: C, 77.90; H, 6.86. Found: C, 77.98; H, 6.90.

1,1-Dicyclopropyl-3-(diphenylphosphinyl)-1,2-butadiene (3dα). Reaction of **1d** and **2α** following the general procedure gave **3dα**: 68% yield, mp 192–193 °C; IR 1955, 1440, 1195 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.9–7.6 (m, 4H), 7.45 (m, 6H), 1.95 (d, *J* = 12.0 Hz, 3H), 1.05 (m, 2H), 0.53 (m, 4H), 0.3 (m, 2H), −0.1 (m, 2H); ^{13}C NMR (CDCl$_3$) δ 207.0 (d, *J*$_{PC}$ = 7.4 Hz) (s), 131.7 (d, *J*$_{PC}$ = 105.0 Hz) (s), 131.6 (d), 131.4 (d), 131.9 (d), 128.0 (d, *J*$_{PC}$ = 12.3 Hz) (d), 111.4 (d, *J*$_{PC}$ = 13.5 Hz) (s), 95.3 (d, *J*$_{PC}$ = 103.5 Hz) (s), 14.6 (d, *J*$_{PC}$ = 8.5 Hz) (d or q), 11.2 (d, *J*$_{PC}$ = 6.2 Hz) (d or q), 5.3 (d, *J*$_{PC}$ = 2.2 Hz) (t); ^{31}P NMR (CDCl$_3$) δ 16.4. Anal. Calcd for C$_{22}$H$_{23}$OP: C, 79.02; H, 6.93. Found: C, 79.12; H, 6.87.

1,1-Diphenyl-3-(diphenylphosphinyl)-1,2-propadiene (3eα). Reaction of **1e** and **2α** following the general procedure gave **3eα**: 67% yield; mp 170–171 °C;[51] IR 1942, 1460, 1440 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.86–7.66 (m, 5 H), 7.66–7.34 (m, 12 H), 7.15–7.11 (m, 3 H), 6.45 (d, *J* = 1.5 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ 206.0 (s), 134.2 (d, *J*$_{PC}$ = 33.0 Hz) (s), 131.0–128.0 (d), 111.0 (s), 88.8 (d, *J*$_{PC}$ = 101.6 Hz) (d).

3-Methyl-1-phenyl-1-(diphenylphosphinyl)-1,2-butadiene (3fα). Reaction of **1f** and **2α** following the general procedure gave **3fα**: 52% yield; mp 125 °C;[52] IR 1951, 1440 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 8.1–7.2 (m, 15H), 1.5 (d, *J* = 6.0 Hz, 6H); ^{13}C NMR (CDCl$_3$) δ 210.0 (s), 132.8 (d, *J*$_{PC}$ = 105.0 Hz) (s), 131.5 (d), 128.3 (d), 100.4 (d, *J*$_{PC}$ = 103.0 Hz) (s), 100.0 (d, *J*$_{PC}$ = 13.6 Hz) (s), 19.0 (d, *J*$_{PC}$ = 10.7 Hz) (q); ^{31}P NMR (CDCl$_3$) δ 30.73; MS *m/z* 344 (99), 329 (12), 286 (13), 201 (100), 155 (24), 143 (67); HRMS calcd for C$_{23}$H$_{21}$OP 344.13299, found 344.1322.

General Procedure of the Addition of Dihalocarbene to Allenic Phosphine Oxides 3. Allenic phosphine oxide **3** (30 mmol), bromoform or chloroform (30 mL) or dibromofluoromethane (10 g), triethylbenzylammonium chloride (200 mg) were stirred at 0 °C. A solution of 50% aqueous NaOH was added dropwise, and stirring was maintained at room tem-

(49) The mechanism shown in Scheme 6 involves an intramolecular nucleophilic substitution of a cyclopropyl bromide by a phosphorus-stabilized propargyl carbanion. For such as nucleophilic displacements, see: Johnson, C. R.; Janiga, E. R. *J. Am. Chem. Soc.* **1973**, *95*, 7692–7700.

(50) Hunt, B. B.; Saunders, B. C. *J. Chem. Soc.* **1957**, 2413–2414.

(51) Simonnin, M.-P.; Borecka, B. *Bull. Soc. Chim. Fr.* **1966**, 3842–3843.

(52) Heydt, H.; Regitz, M. *J. Chem. Res. Miniprint* **1978**, 4248, 4270–4288.

perature. The addition was followed by TLC (silica gel, eluent ether−methanol, 99/1). Aqueous NaOH was added until no more change occurred, even if the allenic phosphine oxide remained. The dark mixture was extracted with CH_2Cl_2, and the solution was washed to neutrality, dried over SO_4Mg, concentrated in vacuo, and chromatographed on silica gel (eluent, ether) to give **4** or **6bα**.

1,1-Dibromo-2,2-dimethyl-3-[(diphenylphosphinyl)-methylidene]cyclopropane (4aα). Reaction of **3aα** and bromoform following the general procedure gave **4aα**: 52% yield; mp 99−100 °C; IR 1438, 1107, 1120 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 8.03−7.7 (4H), 7.56 (m, 6H), 7.06 (d, J = 20 Hz, 1H), 1.36 (s, 6H); ^{13}C NMR (CDCl$_3$) δ 157.2 (d, J_{PC} = 4.0 Hz) (s), 133.3 (d, J_{PC} = 105.0 Hz) (s), 132.3 (d), 131.4 (d, J_{PC} =10.0 Hz) (d), 128.9 (d, J_{PC} = 13.0 Hz) (d), 117.3 (d, J_{PC} =100.0 Hz) (d), 35.2 (d, J_{PC} = 6.0 Hz) (s), 31.3 (d, J_{PC} = 22.0 Hz) (s), 25.2 (q) (2C); ^{31}P NMR (CDCl$_3$) δ 20.01. Anal. Calcd for C$_{18}$H$_{17}$-Br$_2$OP: C, 49.12; H, 3.89. Found: C, 49.22; H, 3.94.

1,1-Dibromo-2,2-dimethyl-3-[1-(diphenylphosphinyl)-ethylidene]cyclopropane (4bα). Reaction of **3bα** and bromoform following the general procedure gave **4bα**: 48% yield; mp 132 °C; IR 1440 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.71−7.47 (m, 10H), 2.18 (d, J = 11.8 Hz, 3H), 1.07 (s, 6H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 149.1 (d, J_{PC} = 14.0 Hz) (s), 132.4 (d), 132.0 (d, J_{PC} = 10.0 Hz) (d), 128.8 (d, J_{PC} = 12.0 Hz) (d), 127.9 (d, J_{PC} = 96.0 Hz) (s), 35.9 (d, J_{PC} = 4.9 Hz) (s), 31.8 (d, J_{PC} = 21.0 Hz) (s), 25.1 (q) (2C), 16.0 (d, J_{PC} = 10.0 Hz) (q); ^{31}P NMR (CDCl$_3$) δ 26.8; MS m/z 456 (6), 454 (16), 452 (6), 375 (27), 373 (24), 294 (33), 293 (39), 201 (100), 183 (25), 181 (19), 169 (29); HRMS calcd for C$_{19}$H$_{19}$OP^{79}Br$_2$ 451.9540, found 451.9563.

1,1-Dibromo-2-[1-[bis-(4-chlorophenyl)phosphinyl]eth-ylidene]-3,3-dimethylcyclopropane (4bβ). Reaction of **3bβ** and bromoform following the general procedure gave **4bβ**: 47% yield; mp 174−175 °C; IR 1440 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.58−7.41 (m, 8H), 2.08 (d, J = 12.1 Hz, 3H), 1.11 (s, 6H); ^{13}C NMR (CDCl$_3$) δ 150.4 (d, J_{PC} = 12.0 Hz) (s), 139.2 (d, J_{PC} = 2.3 Hz) (s), 133.2 (d, J_{PC} = 10.7 Hz) (d), 129.2 (d, J_{PC} = 12.7 Hz) (d), 35.9 (d, J_{PC} = 5.1 Hz) (s), 31.0 (d, J_{PC} = 21.7 Hz) (s), 25.1 (q), 15.9 (d, J_{PC} = 10.5 Hz) (q); ^{31}P NMR (CDCl$_3$) δ 24.8. Anal. Calcd for C$_{19}$H$_{17}$Br$_2$Cl$_2$OP: C, 43.63; H, 3.28. Found: C, 43.70; H, 3.24.

1,1-Dibromo-2-[1-[bis(4-bromophenyl)phosphinyl]eth-ylidene]-3,3-dimethylcyclopropane (4bγ). Reaction of **3bγ** and bromoform following the general procedure gave **4bγ**: 52% yield; IR 1440 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.64−7.60 (m, 4H), 7.51−7.41 (m, 4H), 2.09 (d, J = 12.2 Hz, 3H), 1.13 (s, 6H); ^{13}C NMR (CDCl$_3$) δ 150.5 (d, J_{PC} = 13.5 Hz) (s), 133.3 (d, J_{PC} = 10.8 Hz) (d), 132.2 (d, J_{PC} = 12.6 Hz) (d), 129.9 (d, J_{PC} = 104.0 Hz) (s), 127.8 (d, J_{PC} = 3.4 Hz) (s), 35.9 (d, J_{PC} = 5.1 Hz) (s), 31.0 (d, J_{PC} = 21.6 Hz) (s), 25.2 (q) (2C), 15.9 (d, J_{PC} = 10.4 Hz) (q). Anal. Calcd for C$_{19}$H$_{17}$Br$_4$OP: C, 37.29; H, 2.80. Found: C, 37.35; H, 2.87.

1,1-Dibromo-2-[1-[bis(4-*tert*-butylphenyl)phosphinyl]-ethylidene]-3,3-dimethylcyclopropane (4bδ). Reaction of **3bδ** and bromoform following the general procedure gave **4bδ**: 47% yield; IR 1440 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.54−7.46 (m, 8H), 2.19 (d, J = 11.7 Hz, 3H), 1.27 (s, 18H), 1.01 (s, 6H); ^{13}C NMR (CDCl$_3$) δ 155.7 (d, J_{PC} = 2.7 Hz) (s), 148.0 (d, J_{PC} = 12.0 Hz) (s), 131.8 (d, J_{PC} = 10.3 Hz) (d), 128.1 (d, J_{PC} = 105.7 Hz) (s), 125.7 (d, J_{PC} = 12.4 Hz) (d), 35.7 (d, J_{PC} = 4.7 Hz) (s), 35.0 (s)(2C), 32.0 (d, J_{PC} = 23.0 Hz) (s), 31.2 (q) (6C), 24.9 (q) (2C), 15.9 (d, J_{PC} = 10.0 Hz) (q). Anal. Calcd for C$_{27}$H$_{35}$Br$_2$OP: C, 57.26; H, 6.23. Found: C, 57.18; H, 6.31.

1,1-Dibromo-2-cyclopropyl-2-methyl-3-[1-(diphenyl-phosphinyl)ethylidene]cyclopropane (4cα). Reaction of **3cα** and bromoform following the general procedure gave **4cα**: 52% yield; IR 1440 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.5 (m, 10H), 2.10 (d, J = 12.0 Hz, 3H), 1.4 (s, 3H), 1.4−0.2 (m, 5H); ^{13}C NMR (CDCl$_3$) δ 147.9 (d, J_{PC} = 10.6 Hz) (s), 132.8 (d, J_{PC} = 8 Hz), 131−128 (d), 127.3 (d, J_{PC} = 64.5 Hz) (s), 40.2 (d, J_{PC} = 5.0 Hz) (s), 31.0 (d, J_{PC} = 19.8 Hz) (s), 22.3 (q), 19.1 (d), 16.1 (d, J_{PC} = 10.8 Hz) (q), 6.1 (t), 2.7 (t); ^{31}P NMR (CDCl$_3$) δ 23.93. Anal. Calcd for C$_{21}$H$_{21}$Br$_2$OP: C, 52.53; H, 4.41. Found: C, 52.61; H, 4.36.

1,1-Dibromo-2,2-dicyclopropyl-3-[1-(diphenylphos-phinyl)ethylidene]cyclopropane (4dα). Reaction of **3dα**

and bromoform following the general procedure gave **4dα**: 50% yield; mp 145 °C; IR 1440 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.66−7.46 (m, 10H), 2.02 (d, J = 12.3 Hz, 3H), 1.27 (m, 4H), 0.60−0.30 (m, 4H), 0.17 (m, 2H); ^{13}C NMR (CDCl$_3$) δ 146.1 (s), 131.9 (d), 131.5 (d), 128.6 (d, J_{PC} = 12.2 Hz) (d), 45.9 (d, J_{PC} = 4.5 Hz) (s), 31.9 (d, J_{PC} = 14.6 Hz) (s), 18.7 (d)(2C), 17.1 (d, J_{PC} = 12.8 Hz) (q), 5.50 (t)(2C), 3.03 (t)(2C). Anal. Calcd for C$_{23}$H$_{23}$Br$_2$-OP: C, 54.57; H, 4.58. Found: C, 54.50; H, 4.66.

1,1-Dibromo-2-(diphenylmethylidene)-3-(diphenylphos-phinyl)cyclopropane (4eα). Reaction of **3eα** and bromoform following the general procedure gave **4eα**: 32% yield; mp 159−160 °C; IR 1440 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.68−7.58 (m, 3H), 7.58−7.05 (m, 13H), 7.05−6.96 (m, 4H), 3.32 (d, J = 3.1 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ 141.2 (s), 131.8−127.8 (d), 118.8 (s), 47.9 (d, J_{PC} = 2.0 Hz) (s), 36.6 (d, J_{PC} = 88.0 Hz) (d). Anal. Calcd for C$_{28}$H$_{21}$Br$_2$OP: C, 59.60; H, 3.75. Found: C, 59.71; H, 3.67.

1,1-Dichloro-2,2-dimethyl-3-[1-(diphenylphosphinyl)-ethylidene]cyclopropane (6bα). Reaction of **3bα** and chloroform following the general procedure gave **6bα**: 56% yield; IR 1440 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.73 (m, 10H), 2.26 (d, J = 12.0 Hz, 3H), 1.13 (s, 6H); ^{13}C NMR (CDCl$_3$) δ 147.0 (s), 131.6 (d), 128.5 (d), 89.8 (d, J_{PC} = 105.0 Hz) (s), 60.2 (d, J_{PC} = 22.0 Hz) (s), 35.0 (d, J_{PC} = 5.0 Hz) (s), 22.0 (q) (2C), 16.4 (d, J_{PC} = 10.0 Hz) (q). Anal. Calcd for C$_{19}$H$_{19}$Cl$_2$OP: C, 62.48; H, 5.24. Found: C, 62.55; H, 5.18.

1-Bromo-1-fluoro-2,2-dimethyl-3-[(diphenylphosphin-yl)methylidene]cyclopropane (5aα). Allenic phosphine oxide **3aα** (2.6 g, 10 mmol), dibromofluoromethane (3.3 g, 16 mmol), and triethylbenzylammonium chloride (50 mg) were stirred at room temperature. A solution of 50% aqueous NaOH (2 g) was added dropwise. After 3 h, the mixture was extracted with CH_2Cl_2, and the solution was washed to neutrality, dried over SO_4Mg, concentrated in vacuo, and chromatographed on silica gel (eluent, ether). The yield (about 20%) was very low, and no further attempts were done to improve it. **5aα**: IR 1440 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.59 (m, 4H), 7.38 (m, 10H), 6.98 (d, J = 21.6 Hz, 1H), 1.09 (br s, 6H); ^{13}C NMR (CDCl$_3$) δ 152.9 (s), 133.1 (d, J_{PC} = 1.9 Hz) (d), 132.0 (d, J_{PC} = 2.6 Hz) (d), 130.9 (d, J_{PC} = 10.0 Hz) (d), 128.5 (d, J_{PC} = 12.3 Hz) (d), 118.2 (d, J_{PC} = 98.0 Hz) (d), 81.8 (d, J_{FC} = 315 Hz, d, J_{PC} = 24.0 Hz) (s), 33.7 (d, J_{FC} = 11.8 Hz, d, J_{PC} = 6.8 Hz) (s), 24.0 (q), 17.9 (d, J_{PC} = 5.6 Hz) (q); ^{31}P NMR (CDCl$_3$) δ 20.0. Anal. Calcd for C$_{18}$H$_{17}$BrFOP: C, 57.01; H, 4.52. Found: C, 56.86; H, 4.61.

1-Bromo-1-(diphenylphosphinyl)-3-methyl-1,2-butadi-ene (7aα). Phosphine oxide **3aα** (2.7 g, 10 mmol), CH$_2$Br$_2$ (6.9 g, 40 mmol), CBr$_2$F$_2$ (8.4 g, 40 mmol), KOH (4.5 g, 80 mmol), water (7.4 mL), and tetrabutylammonium sulfate (0.34 g, 1 mmol) were stirred during 24 h. After extraction with CH_2Cl_2, the solution was washed to neutrality, dried over SO_4Mg, concentrated in vacuo, and chromatographed on silica gel (eluent, ether) to give 2.1 g (60% yield) of **7aα**. A similar result was obtained when **3aα** was stirred only with CBr$_2$F$_2$. **7aα**: mp 98−99 °C;[26] IR 1951, 1440, 1210, 1020 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.64−7.51 (m, 4H), 7.32−7.25 (m, 6H), 1.39 (m, 6H); ^{13}C NMR (CDCl$_3$) δ 206.0 (s), 131.9 (d, J_{PC} = 2.55 Hz) (d), 131.3 (d, J_{PC} = 9.7 Hz) (d), 130.4 (d, J_{PC} = 11.0 Hz) (d), 129.9 (d, J_{PC} = 110 Hz) (s), 128.0 (d, J_{PC} = 12.6 Hz) (d), 108.0 (d, J_{PC} = 9.5 Hz) (s), 79.6 (d, J_{PC} = 117.6 Hz) (s), 19.0 (q); ^{31}P NMR (CDCl$_3$) δ 25.8; MS m/z 348 (23), 346 (23), 268 (20), 267 (100), 201 (82), 143 (68), 128 (22); HRMS calcd for C$_{17}$H$_{16}$OP^{79}Br 346.01220, found 346.0112, calcd for [M − Br]$^+$ 267.09387, found 267.0936.

General Procedure for the Reaction of *n*-Butyllithium with *gem*-Dibromocyclopropanes 4. To a stirred and cooled (−90 °C) solution of *gem*-dibromocyclopropane **4** (2 mmol) in anhydrous THF (15 mL) under argon was added *n*-BuLi (1.6 M in hexane, 1.4 mL). After 1 h, the mixture was allowed to warm slowly to room temperature overnight. After hydrolysis and extraction with CH_2Cl_2, the organic layers were washed to neutrality and dried over SO_4Mg. The solvent was eliminated in vacuo and the crude product chromatographed on silica gel (eluent, ether to ether−methanol, 98/2).

1-(Diphenylphosphinyl)-4-methyl-3-penten-1-yne (8). Reaction of **4aα** and *n*-BuLi following the general procedure gave **8**: 35% yield; IR 2140, 1435, 1200, 1115 cm^{-1}; ^{1}H NMR

(CDCl$_3$) δ 7.87−7.75 (m, 4H), 7.48−7.38 (m, 6H), 5.42 (br. s, 1H), 1.93 (s, 3H), 1.85 (s, 3H); ^{13}C NMR (CDCl$_3$) δ 157.2 (s), 135.0 (s), 132.0 (d), 131.0 (d), 128.5 (d), 104.6 (d, J_{PC} = 30.0 Hz) (s), 103.6 (d, J_{PC} = 4.0 Hz) (d), 25.3 (q), 21.9 (q). Anal. Calcd for C$_{18}$H$_{17}$OP: C, 77.13; H, 6.11. Found: C, 77.07; H, 6.10.

2-Cyclopropyl-5-(diphenylphosphinyl)-2,3,4-hexatriene (10a). Reaction of **4c**α and *n*-BuLi following the general procedure gave **10a**: 45% yield; IR 2061, 1441 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.7 (m, 4H), 7.36 (m, 6H), 2.03 (d, J = 12.5 Hz, 3H), 1.3 (br s, 3H), 0.75 (m, 2H), 0.6 (m, 2H); ^{13}C NMR (CDCl$_3$) δ (minor isomer) 167.5 (d, J_{PC} = 8.0 Hz) (s), 150.0 (d, J_{PC} = 7.0 Hz) (s), 92.7 (d, J_{PC} = 103.6 Hz) (s), 21.7 (d, J_{PC} = 6.0 Hz) (q), 17.6 (d, J_{PC} = 4.0 Hz) (q), 8.8 (t); (major isomer) 167.9 (d, J_{PC} = 9.0 Hz) (s), 150.1 (d, J_{PC} = 6.0 Hz) (s), 132.4 (d, J_{PC} = 7.0 Hz) (s), 131.6 (d, J_{PC} = 105.0 Hz) (s), 131−127 (d), 99.9 (d, J_{PC} = 107.0 Hz) (s), 21.1 (d, J_{PC} = 6.6 Hz) (q), 18.1 (d, J_{PC} = 6.6 Hz) (q), 17.3 (d, J_{PC} = 3.9 Hz) (q), 8.9 (t). Anal. Calcd for C$_{21}$H$_{21}$OP: C, 78.73; H, 6.61. Found: C, 78.79; H, 6.68.

1,1-Dicyclopropyl-4-(diphenylphosphinyl)-2,3,4-pentatriene (10b). Reaction of **4d**α and *n*-BuLi following the general procedure gave **10b**: 40% yield; IR 2060, 1440, 1180 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.7 (m, 4H), 7.4 (m, 6H), 2.2 (d, J = 9.8 Hz, 3H), 1.6−1.1 (m, 4H), 0.83 (m, 2H), 0.5 (m, 4H); ^{13}C NMR (CDCl$_3$) δ 167.4 (d, J_{PC} = 9.0 Hz) (s), 144.0 (d, J_{PC} = 13.0 Hz) (s), 141.8 (d, J_{PC} = 8.0 Hz) (s), 131.2 (d), 127.9 (d), 127.8 (d), 127.7 (d), 97.7 (d, J_{PC} = 107.0 Hz) (s), 17.9 (d, J_{PC} = 8.5 Hz) (q), 16.5 (d, J_{PC} = 13.8 Hz) (d), 16.4 (d, J_{PC} = 13.7 Hz) (d), 9.4 (t), 9.3 (t); ^{31}P NMR (CDCl$_3$) δ 28.7. Anal. Calcd for C$_{23}$H$_{23}$OP: C, 79.75; H, 6.69. Found: C, 79.68; H, 6.76.

(3S*)-(E)-2-[1-(Diphenylphosphinyl)ethylidene]-5-[(S*)-2-(diphenylphosphinyl)prop-1-enylidene]-1,1,4,4-tetramethylspiro[2.2]pentane (14α). Reaction of **4b**α and *n*-BuLi following the general procedure gave **14α**: 52% yield; mp 78 °C; IR 3050, 1990, 1440 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.8−7.2 (m, 20H), 1.97 (d, J = 11.6 Hz, 3H), 1.36 (d, J = 12.2 Hz, 3H), 1.34 (s, 3H), 1.0 (s, 3H), 0.83 (s, 3H), 0.81 (s, 3H); ^{13}C NMR (CDCl$_3$) δ 188.2 (d, J_{PC} = 9.0 Hz) (s), 151.7 (d, J_{PC} = 11.0 Hz) (s), 131.5 (d), 128.2 (d), 116.5 (d, J_{PC} = 99.0 Hz) (s), 95.4 (d, J_{PC} = 106.0 Hz) (s), 93.0 (d, J_{PC} = 14.0 Hz) (s), 40.1 (d, J_{PC} = 20.0 Hz, d, J_{PC} = 5.3 Hz) (s), 35.03 (d, J_{PC} = 3.7 Hz) (s), 27.0 (t, J_{PC} = 2.8 Hz) (s), 23.5 (q), 22.9 (q), 22.1 (q), 20.3 (q), 18.2 (d, J_{PC} = 12.6 Hz) (q), 15.5 (d, J_{PC} = 7.5 Hz) (q); ^{31}P NMR (CDCl$_3$) δ 30.46 and 27.80; MS *m/z* 588 (2), 573 (2), 467 (2), 388 (7), 387 (44), 386 (29), 371 (27), 202 (47), 201 (100), 185 (55), 184 (77), 170 (18), 169 (16), 155 (15); HMRS calcd for C$_{38}$H$_{38}$O$_2$P$_2$ 588.23469, found 588.2339.

(3S*)-2-[1-[Bis(4-chlorophenyl)phosphinyl]ethylidene]-5-[(S*)-2-[bis(4-chlorophenyl)phosphinyl]prop-1-enylidene]-1,1,4,4-tetramethylspiro[2.2]pentane (14β). Reaction of **4b**β and *n*-BuLi following the general procedure gave **14β**: 68% yield; IR 1995 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.63−7.19 (m, 16H), 1.95 (d, J = 11.9 Hz), 1.378 (d, J = 12.4 Hz, 3H), 1.374 (s, 3H), 1.09 (s, 3H), 0.92 (s, 3H), 0.917 (s, 3H); ^{13}C NMR (CDCl$_3$) δ 188.6 (d, J_{PC} = 9.0 Hz) (s), 153.3 (d, J_{PC} = 11.0 Hz) (s), 138.9 (s), 133.2 (d, J_{PC} = 11.0 Hz) (d), 129.3−128.8 (d), 115.9 (d, J_{PC} = 101.0 Hz) (s), 95.3 (d, J_{PC} = 108.0 Hz) (s), 93.46 (d, J_{PC} = 13.0 Hz) (s), 40.6 (d, J_{PC} = 18.9 Hz, d, J_{PC} = 5.1 Hz) (s), 35.8 (d, J_{PC} = 3.7 Hz) (s), 27.6 (s), 23.9 (q), 23.1 (q), 22.4 (q). Anal. Calcd for C$_{38}$H$_{34}$Cl$_4$O$_2$P$_2$: C, 62.83; H, 4.72. Found: C, 62.87; H, 4.81.

(3S*)-(E)-2-[1-[Bis(4-bromophenyl)phosphinyl]ethylidene]-5-[(S*)-2-[bis(4-bromophenyl)phosphinyl]prop-1-enylidene]-1,1,4,4-tetramethylspiro[2.2]pentane (14γ). Reaction of **4b**γ and *n*-BuLi following the general procedure gave **14γ**: 41% yield; mp 133−134 °C; IR 1995, 1580, 1480, 1205 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.41−7.32 (m, 16H), 1.78 (d, J = 11.8 Hz, 3H); ^{13}C NMR (CDCl$_3$) δ 188.1 (d, J_{PC} = 9.0 Hz) (s), 152.8 (d, J_{PC} = 12.7 Hz) (s), 133−131 (d), 114.7 (d, J_{PC} = 100.0 Hz) (s), 94.9 (d, J_{PC} = 107.0 Hz) (s), 93.0 (d, J_{PC} = 15.0 Hz) (s), 40.2 (d, J_{PC} = 19.3 Hz, d, J_{PC} = 5.4 Hz) (s), 35.3 (d, J_{PC} = 3.8 Hz) (s), 27.1 (d, J_{PC} = 6.2 Hz, d, J_{PC} = 3.0 Hz) (s), 23.8 (q), 23.0 (q), 22.3 (q), 20.6 (q), 18.1 (d, J_{PC} = 12.9 Hz), 15.2 (d, J_{PC} = 8.1 Hz). Anal. Calcd for C$_{38}$H$_{34}$Br$_4$O$_2$P$_2$: C, 50.47; H, 3.79. Found: C, 50.59; H, 3.74.

(3S*)-(E)-2-[1-[Bis(4-tert-butylphenyl)phosphinyl]ethylidene]-5-[(S*)-2-[bis(4-tert-butylphenyl)phosphinyl]prop-1-enylidene]-1,1,4,4-tetramethylspiro[2.2]pentane (14δ). Reaction of **4b**δ and *n*-BuLi following the general procedure gave **14δ**: 58% yield; mp 130−132 °C (AcOEt−ligroin); IR 1998, 1605, 1190 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.6−7.23 (m, 16H), 1.90 (d, J = 11.3 Hz, 3H), 1.39 (d, J = 11.9 Hz, 3H), 1.23 (s), 1.21 (s), 1.18 (s), 1.13 (s) (1.23 to 1.13, 39H), 0.92 (s, 3H), 0.66 (s, 6H); ^{13}C NMR (CDCl$_3$) δ 188.2 (d, J_{PC} = 9.2 Hz) (s), 155.1 (d, J_{PC} = 2.6 Hz) (s), 154.8 (d, J_{PC} = 15.0 Hz) (s), 154.6 (d, J_{PC} = 2.8 Hz) (s), 150.6 (d, J_{PC} = 14.3 Hz) (s), 131.8 (d, J_{PC} = 4.1 Hz) (d), 131.5 (d, J_{PC} = 9.6 Hz) (d), 131.4 (d, J_{PC} = 15.3 Hz) (d), 129.9 (d, J_{PC} = 107.6 Hz) (s), 129.1 (d, J_{PC} = 104.5 Hz) (s), 129.0 (d, J_{PC} = 104 Hz) (s), 128.2 (d, J_{PC} = 105.9 Hz) (s), 125.3 (d, J_{PC} = 12.0 Hz) (d), 125.2 (d, J_{PC} = 12.3 Hz) (d), 117.4 (d, J_{PC} = 100.4 Hz) (s), 96.0 (d, J_{PC} = 105.7 Hz) (s), 92.7 (d, J_{PC} = 14.8 Hz) (s), 39.6 (d, J_{PC} = 19.3, d, J_{PC} = 5.6 Hz) (s), 34.8 (s), 34.7 (s), 31.0 (q), 26.9 (d, J_{PC} = 5.8, d, J_{PC} = 2.9 Hz) (s), 23.7 (q), 23.0 (q), 22.0 (q), 20.3 (q), 18.5 (d, J_{PC} = 12 Hz) (q), 15.7 (d, J_{PC} = 7.8 Hz) (q).

X-ray Crystallography of C$_{54}$H$_{70}$P$_2$O$_2$ (14δ).[53] C$_{54}$H$_{70}$O$_2$P$_2$: M_r = 813.11, triclinic, $P\bar{1}$, a = 11.934(6) Å, b = 12.521(3) Å, c = 20.560(5) Å, α = 82.13(2)°, β = 78.23(3)°, γ = 71.11(3)°, V = 2837(2) Å^{-3}, Z = 2, D_x = 0.952 mg·m^{-3}, λ(Mo Kα) = 0.709 26 Å, μ = 1.05 cm^{-1}, F(000) = 880, T = 294 K, final R = 0.074 for 3919 observations. The sample (0.25 × 0.25 × 0.40 mm) is studied on an automatic diffractometer (Enraf-Nonis CAD-4) with graphite monochromatized Mo Kα radiation. The cell parameters are obtained by fitting a set of 25 high-θ reflections. The data collection (2θ$_{max}$ = 50°, scan ω/2θ = 1, t_{max} = 60 s, range *hkl*: *h* 0.14, *k* −14.14, *l* −24.24, intensity controls without appreciable decay (0.3%) gives 9443 reflections from which 3919 independent (R_{int} = 0.011) with I > 5σ(*I*). After Lorenz and polarization corrections the structure was solved with direct methods which reveal many non-hydrogen atoms of the molecule. The remaining ones, in particular the disordered carbon atoms of the *tert*-butyl groups, are found after successive scale factor calculations and Fourier difference. After isotropic (R = 0.11), then anisotropic refinement (R = 0.098), many hydrogen atoms may be found with a Fourier difference. The whole structure was refined by the full-matrix least-squares techniques (use of F magnitude; *x*, *y*, *z*, β_{ij} for P, C, and O atoms, *x*, *y*, *z*, B_{iso} for *tert*-butyl C atoms, and *x*, *y*, *z* fixed for H atoms; 506 variables and 3919 observations; ω = 1/σ(F_o)^2 = [σ^2(*I*) + (0.04F_o^2)^2]$^{-1/2}$ with the resulting R = 0.076, R_w = 0.074 and S_w = 1.82 (residual Δρ ≤ 0.42 e Å^{-3}).[54] Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). All the calculations were performed on a Digital MicroVAX 3100 computer with the MOLEN package.[55]

Supporting Information Available: Tables of selected bond lengths and angles for **14δ** (1 page). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(53) The authors have deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K.

(54) *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, 1974; present distributor, D. Reidel: Dordrecht.

(55) Fair, C. K. *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*; Enraf-Nonius: Delft, The Netherlands, 1990.