Table III. Summary of Crystallographic Data

formula	$[C_{18}H_{28}ORhS][CF_3O_3S]$	$[C_{19}H_{30}ORhS][CF_3O_3S]$
crystal system	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
a, Å	8.618 (3)	8.986 (2)
b, Å	18.192 (3)	9.343 (2)
c, Å	14.209 (5)	14.745 (4)
α, deg	90	92.920 (7)
β, deg	96.39 (1)	107.510 (7)
γ, deg	90	94.214 (8)
Z	4	2
V, Å^3	2214 (2)	1173.9 (8)
density (calcd), g/cm^{-3}	1.633	1.580
color	orange-yellow	orange
dimensions, mm	0.2 × 0.3 × 0.4	0.2 × 0.2 × 0.4
temp, °C	−40	−30
diffractometer	Syntex $P2_1$	Syntex $P2_1$
radiation	Mo Kα	Mo Kα
μ, cm^{-1}	9.86	9.31
transmission factor range	0.813–0.760	0.874–0.800
2θ limit	$3° < 2\theta < 46°$	$3° < 2\theta < 50°$
no. of reflcns measured	3563	5169
no. of unique reflcns	2891	4037
no. of reflcns with $I > 2.58\sigma(I)$	2542	3791
R	0.034	0.041
R_w	0.049	0.063
$\Delta(\rho)$, e Å^{-3}	$0.53 > \Delta(\rho) > -0.71$	$1.63 > \Delta(\rho) > -0.76$

crystal was approximately bound by the {0 0 1} and {2 0 −1} forms and the (1 4 −4) and (0 −1 1) faces. Distances from the crystal center to these facial boundaries were 0.09, 0.22, 0.09, and 0.10 mm, respectively.

The structure was solved by direct methods (SHELXS-86); the correct rhodium atom position was deduced from the *E*-map. Subsequent least-squares refinements and difference Fourier syntheses revealed positions for the remaining non-hydrogen atoms. Hydrogen atoms were included as fixed contributors in idealized positions. In the final cycle of least-squares refinement, anisotropic thermal coefficients were refined for non-hydrogen atoms and a common isotropic thermal parameter was varied for hydrogen atoms. Successful convergence was indicated by the maximum shift/error for the last least-squares cycle. The highest peak in the final difference Fourier map was in the vicinity of the anion and the only other peaks above background were in the vicinity of the rhodium atom; the final map had no other significant features. An analysis of variance between observed and calculated structure factors showed a slight dependence on sin (Θ). Refinement in the acentric space group $P1$ converged with significant differences between chemically equivalent bond lengths and failed to significantly improve the weighted residual. Average values of the normalized structure factors supported the acentric choice which was ultimately rejected on the basis of refinements. Bond lengths and angles for the $CF_3SO_3^-$ ion reflected excessive thermal motion and possibly disorder. Attempts to describe a disordered model for this ion were not successful.

Acknowledgment. This research was sponsored by the U.S. Department of Energy through Grant No. DE-FO2-9ER14146. Johnson Mathey is thanked for the loan of precious metals. We thank Dr. Vera Mainz and her staff at the Molecular Spectroscopy Laboratory for assistance with the variable-temperature NMR experiments and Dr. Paul Brandt for the gift of the tetramethylcyclopentadiene. We thank Shifang Luo and Harald Krautscheid for helpful discussions.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, bond angles and distances for $[(C_5Me_5)Rh(C_4Me_4S\text{-}2\text{-}OH)]OTf$ and $[(C_5Me_5)Rh(MeSC_3Me_3COMe)]OTf$ (10 pages); listing of structure factors (43 pages). Ordering information is given on any current masthead page.

General Approaches to Phosphinidenes via Retroadditions

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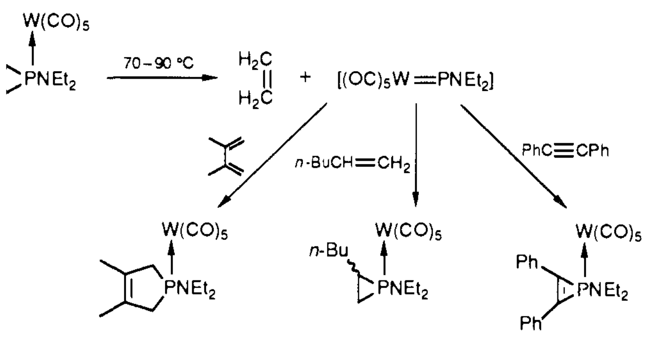
Received April 6, 1992

Abstract: The retroaddition strategy for the generation of phosphinidenes involves thermal and photochemical decomposition of 1-arylphosphiranes and photolysis of 1-aryl-3-phospholenes. Evidence that free phosphinidenes are produced as reactive intermediates includes a lack of dependence of the conversion rate on precursor and substrate concentrations and the nature of the reaction products. These are best rationalized by the addition of phosphinidenes to carbon–carbon π-bonds forming three-membered rings and the dimerization of phosphinidenes to diphosphenes.

The novelty and synthetic utility of the reactions of species containing subvalent six-electron neutral atoms have led to a wide interest in the chemistry of carbenes,[1] nitrenes,[2] silylenes,[3] and, more recently, germylenes.[4] Despite considerable effort,[5] little is known about the monovalent phosphorus species, phosphinidenes, largely for want of general routes to them. Indeed, Mathey has voiced skepticism toward the entire enterprise: "...generation of these transient phosphinidenes is deduced from the isolation of products whose formation can be explained by a mechanism involving such intermediates. However, in almost every case, it is possible to conceive alternate mechanisms which do not involve phosphinidenes."[5]

A striking difference between the chemistry of carbenes and that of their silicon and germanium analogs is that virtually every silylene and germylene reaction is *reversible*. Having generated silylenes and germylenes by extrusion from their familiar addition

Scheme I



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[*] Author to whom correspondence should be addressed. This work was carried out with financial support from the National Science Foundation under Grant No. CHE-9108130.

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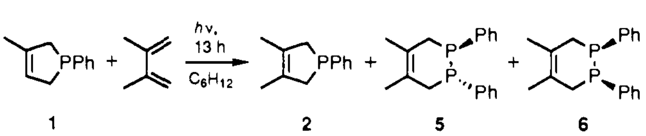
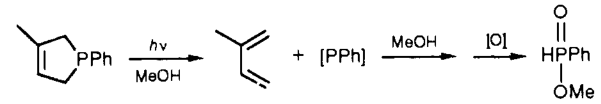
Scheme II



ratio	conversion	yields		
1:1	31%	13%	26%	17%
1:3	34%	16%	19%	14%
1:5	28%	18%	16%	13%
1:10	32%	18%	18%	14%

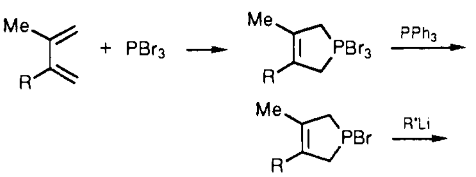
products silacyclopent-3-enes,[6] siliranes,[7,8] and germacyclopent-3-enes,[9] it was reasonable to adopt a retroaddition strategy for the generation of phosphinidenes via the decomposition of 3-phospholenes and phosphiranes.

There is some precedent for the use of 3-phospholenes as phosphinidene precursors. Tomioka obtained a product interpreted as resulting from the oxidation of a phosphinidene–methanol adduct, when 3-methyl-1-phenyl-3-phospholene was irradiated in methanol under nitrogen.[10]



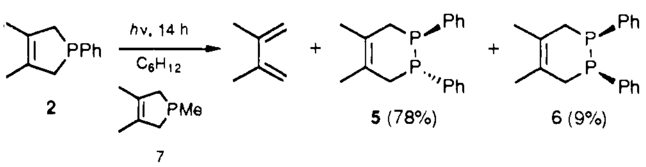
Phosphirane–metal complexes have been shown by Mathey and co-workers to undergo thermal decomposition under mild conditions, liberating phosphinidene complexes whose adducts have been isolated (Scheme I).[11] It is the absence of evidence for such addition reactions in most previous attempts to produce free phosphinidenes that has led to skepticism regarding their success.

The 3-phospholenes whose photochemical decomposition are reported here were synthesized by the route of Myers and Quin:[12]



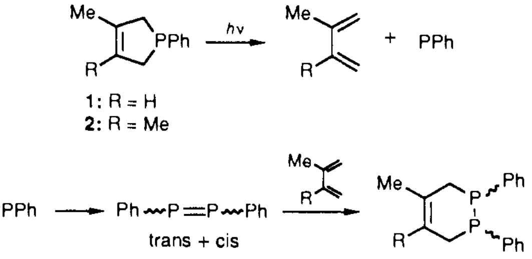
1: R = H, R′ = Ph
2: R = Me, R′ = Ph
3: R = Me, R′ = Mes
4: R = Me, R′ = Mes*

Photolysis at 254 nm of 3,4-dimethyl-1-phenyl-3-phospholene (2)[13] in cyclohexane solution led to a high yield of a mixture of *trans*- and *cis*-4,5-dimethyl-1,2-diphenyl-1,2-diphosphacyclohex-4-enes (5 (78%) and 6 (9%)).[14,15] The presence of 1,3,5-trimethyl-3-phospholene (7) does not lead to new products.



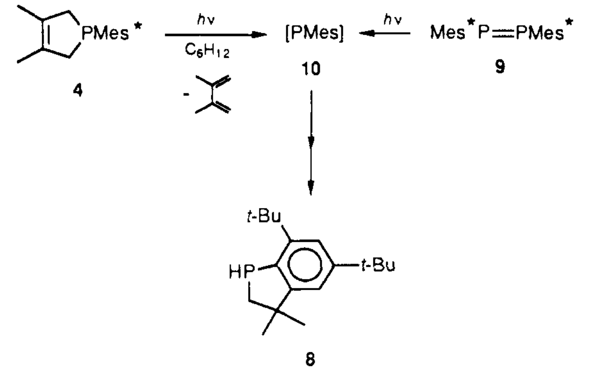
Irradiation of 3-methyl-1-phenyl-3-phospholene (1)[16,17] in the presence of 2,3-dimethylbutadiene leads to the same diphenyldiphosphacyclohexenes 5 and 6 and to 3,4-dimethyl-1-phenyl-3-phospholene (2) (Scheme II). The conversion of the initial phospholene 1 does not depend on the concentration of diene substrate, but the ratio of the yields of phospholene 2 and disphosphacyclohexene products 5 and 6 increases with increasing diene substrate concentration.

These results are consistent with the photoextrusion of phenylphosphinidene, C_6H_5P, whose addition to a diene yielding a 3-phospholene competes with dimerization to a mixture of *cis*- and *trans*-1,2-diphenyldiphosphene, PhP=PPh. Addition of a diphosphene to a diene gives a diphosphacyclohexene.



If the diphosphacyclohexene products had resulted from photodimerization of phospholene molecules or from attack of phenylphosphinidene on a phospholene molecule, diphosphacyclohexenes containing a CH_3P unit would be expected when an arylphospholene is irradiated in the presence of 1,3,5-trimethyl-3-phospholene (7). If a photoexcited phospholene reacted with a diene to form either five- or six-membered ring products, the conversion would be expected to depend on the diene concentration.

Another form of indirect evidence for the photoextrusion of a phosphinidene comes from the irradiation of 3,4-dimethyl-1-supermesityl-3-phospholene (4). The major product is the same phosphaindan 8 obtained by Yoshifuji and co-workers from photolysis of disupermesityldiphosphene (9), for which a supermesitylphosphinidene intermediate (10) was suggested.[18,19]



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(3) Gaspar, P. P. *Ibid.* **1978**, *1*, 229; **1981**, *2*, 335; **1985**, *3*, 333.

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(9) Lei, D.; Gaspar, P. P. *Polyhedron* **1991**, *10*, 1221.

(10) Tomioka, H.; Nakamura, S.; Ohi, T.; Izawa, Y. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 3707.

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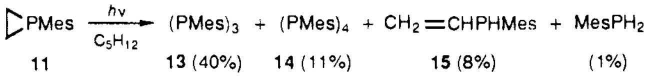
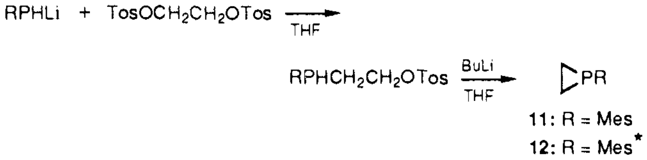
(17) Quin, L. D.; Breen, J. J.; Myers, D. *J. Org. Chem.* **1971**, *36*, 1297.

Scheme III



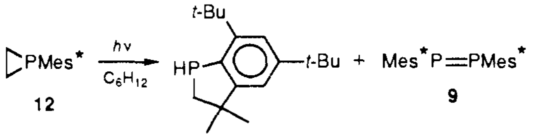
The mesityl- and supermesitylphosphiranes (**11** and **12**) whose decompositions were studied were synthesized by modification of the sequence devised by Oshikawa and Yamashita:[20]



The 254-nm photolysis of mesitylphosphirane (**11**) is not accelerated by the presence of a variety of reaction substrates and does not depend on their concentrations (Scheme III). In the absence of added substrates, the major products are formal oligomers of mesitylphosphinidene, the known compounds cyclo-$(MesP)_3$ (**13**) and cyclo-$(MesP)_4$ (**14**),[16] with a low yield of vinylphosphine **15** believed to result from ring-opening of the phosphirane. In the presence of olefins, dienes, and alkynes, the yield of phosphinidene oligomers drops and three-membered rings are obtained.[21] Vinylphosphiranes are known to undergo photorearrangement; therefore the phospholene **3** obtained in 33% yield from irradiation of 1-mesitylphosphirane (**11**) in the presence of 2,3-dimethylbutadiene may be a transformation product of the vinylphosphirane **16** (Scheme IV).[22] Pyrolysis of mesitylphosphirane (**11**) at 190 °C in the presence of 2,3-dimethylbutadiene (Scheme IV) leads to a 70% yield of phospholene **3**, and no vinylphosphirane **16** is found.

Only one claim has previously been made for the addition of an uncomplexed phosphinidene to an olefin,[23] and there is no previous report of addition to an alkyne (Scheme V).

The irradiation of supermesitylphosphirane (**12**) in the presence of a variety of olefins, dienes, and an alkyne, gives only the phosphaindan product **8** (in yields up to 68%) believed to result from the intramolecular reaction of supermesitylphosphinidene, Mes*P, (**10**), but ultraviolet and ^{31}P NMR spectra of the reaction mixture indicate the presence of low ($<10^{-4}$ M) concentrations of the phosphinidene dimer, the Yoshifuji diphosphene **9**.[24]



8 60%

In summary, no free phosphinidene has been detected directly in these experiments, and, heeding Mathey's warning, spectroscopic and quantitative kinetic studies are needed on the decomposition of the phospholenes and phosphiranes employed as precursors. However, these decompositions appear to be first order, and the reaction products are in accord with the formation of free arylphosphinidenes as reactive, product-forming intermediates. These results suggest that addition of phosphinidenes to carbon–carbon π-bonds forming three-membered phosphacycles is a general and synthetically useful reaction. Photochemical and thermal extrusion reactions from easily accessible 3-phospholenes and phosphiranes promise to make available a wide range of phosphinidenes for study and for use as synthetic reagents.[25]

Experimental Section

General Data. All preparative reactions were carried out in flame-dried glassware under an atmosphere of dry nitrogen or argon. Unless otherwise specified, photolyses were carried out in a Rayonet RS photochemical reactor equipped with low-pressure mercury lamps emitting 254-nm radiation. All solvents were dried and distilled just prior to use. ^{31}P NMR spectra were recorded at 121 MHz on a Varian XL-300 FT spectrometer employing H_3PO_4 as external standard; ^1H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively, on Varian XL-300 and Gemini-300 FT spectrometers with Me_4Si as external standard. Combined gas chromatography–mass spectrometry was performed on a Finnigan 3200 mass spectrometer and a Hewlett-Packard 5971 GCMS system. Combined gas chromatography–infrared spectroscopy was performed with a Hewlett-Packard 5965A infrared detector. High resolution mass spectra were recorded on a VG-ZAB-SE double-focusing mass spectrometer. Mass spectra were calibrated against perfluoroalkane internal standards. Ultraviolet spectra were recorded on a Cary-219 ultraviolet spectrometer. Analytical gas chromatography was carried out on a Hewlett-Packard 5890 Series II instrument with a flame ionization detector employing a 30-m × 0.32-mm capillary column with a methylpolysiloxane bonded phase.

Recorded yields are based on the unrecovered phosphinidene precursors and were determined by integration of the ^{31}P NMR spectra, using 1,3,4-trimethyl-3-phospholene or trimethyl phosphate ($(MeO)_3PO$) internal standards.

Materials. 2-Bromomesitylene (Aldrich, 99%), 1,3,5-tri-*tert*-butylbenzene (Aldrich, 97%), *n*-butyllithium (1.6 M in hexane, Aldrich), ethylene glycol ditosylate (Aldrich, 97%), lithium aluminum hydride (Aldrich, 95%), magnesium turnings (Aldrich, 98%), phenylsilane (Petrarch), trimethyl phosphate (Aldrich, 97%), and phosphorus tribromide (Aldrich, 97%) were used as received. Cyclohexene (Aldrich, 99%), 3-hexyne (Aldrich, 99%), isoprene (Aldrich, 99%), 2,3-dimethyl-1,3-butadiene (Aldrich, 98%), phosphorus trichloride (Aldrich, 98%), and styrene (Aldrich, 99%) were distilled before use.

1-Bromo-3-methyl-3-phospholene and 1-Bromo-3,4-dimethyl-3-phospholene. These bromophospholenes were prepared by reduction of cycloadducts from phosphorus tribromide and the corresponding diene using the procedure of Hall et al.[13] and Quin et al.[16] 1-Bromo-3-dimethyl-3-phospholene: ^{31}P NMR (C_6D_6) δ 119.7 (lit.[17] (neat) δ 120.5); ^1H NMR (C_6D_6) δ 1.49 (br s, 3 H, Me), 2.43 (d, 2 H, J = 20.9 Hz, CH_2), 2.61 (d, 2 H, J = 20.9 Hz, CH_2), 5.14 (br s, 1 H, CH). An inseparable impurity, 9% 1-bromo-3-methyl-2-phospholene,[12] was detected via its ^{31}P NMR signal at δ 128.9 (lit.[12] 130.6). 1-Bromo-3,4-dimethyl-3-phospholene: bp 100 °C (22 Torr) (lit.[13] bp 103 °C (26 Torr)); ^{31}P NMR (C_6D_6) δ 105.5 (lit.[14] 104.9); ^1H NMR (C_6D_6) δ 1.42 (br s, 6 H, Me), 2.62 (br d, 4 H, J = 20.1 Hz, CH_2) (lit.[14] δ 1.37 (s, 6 H), 2.60 (m, 4 H)).

3-Methyl-1-phenyl-3-phospholene Oxide and 3,4-Dimethyl-1-phenyl-3-phospholene Oxide.[13,16] 1-Bromo-3,4-dimethyl-3-phospholene (4.5 g, 23 mmol) in 10 mL of THF (dried over Na) was added dropwise to an ice-cooled flask containing phenylmagnesium bromide prepared from bromobenzene (4.8 g, 31 mmol) and magnesium turnings (0.78 g, 0.032 g atom) in 100 mL of THF. The mixture was allowed to warm to room temperature and stirred overnight and then hydrolyzed with 30 mL of 10% aqueous NH_4Cl and stirred 1 h. The organic layer was separated and the aqueous layer extracted with 60 mL of ether. The combined organic phase were dried over Na_2SO_4, the solvents evaporated, and the product distilled yielding 3,4-dimethyl-1-phenyl-3-phospholene oxide (4.1 g, 86%), bp 163–165 °C (0.15 Torr): ^{31}P NMR (C_6D_6) δ 47.9; ^1H NMR (C_6D_6) δ 1.40 (br s, 6 H, Me), 2.28 (m, 2 H, CH_2), 2.65 (m, 2 H, CH_2), 7.15 (m, 3 H, *o*-, *p*-phenyl), 7.75 (m, 2 H, *m*-phenyl). 3-Methyl-1-phenyl-3-phospholene oxide was synthesized by the same procedure in 81% yield: ^{31}P NMR (C_6D_6) δ 58.4. A 9% impurity of 3-methyl-1-phenyl-2-phospholene oxide was detected by ^{31}P NMR (C_6D_6), δ 62.7.

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(18) Yoshifuji, M.; Sato, T.; Inamoto, N. *Chem. Lett.* **1988**, 1735.

(19) We repeated the photolysis of the Yoshifuji diphosphene with 254-nm radiation at ambient temperature and also obtained the phosphaindan as the major product.

(20) Oshikawa, T.; Yamashita, M. *Synthesis* **1985**, 290.

(21) 1-Mesitylphosphiranes have also been obtained by addition of mesitylphosphinidene (MesP) to 1-pentene and cyclooctene.

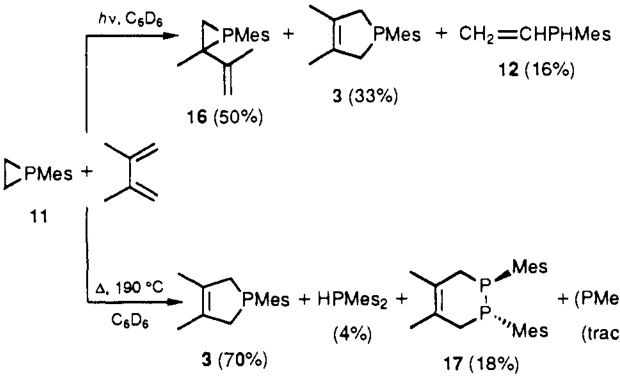
(22) Richter, W. J. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 292; *Chem. Ber.* **1983**, *116*, 3293.

(23) Fritz, G.; Vaahs, T.; Fleischer, H.; Matern, E. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 315.

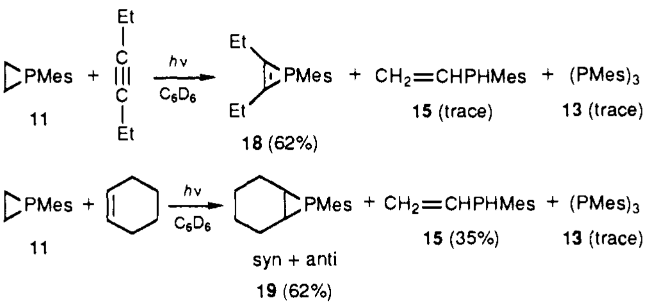
(24) It appears from the shift in the absorption maximum for the diphosphene with increasing irradiation time that *cis*-diphosphene is formed initially and is converted to *trans*-diphosphene in the course of the reaction. Partial trans-to-cis isomerization of the diphosphene has been reported to shift the λ_{max} at 347 nm to 343 nm: Caminade, A.-M.; Verrier, M.; Ades, C.; Paillous, M.; Koenig, M. *J. Chem. Soc., Chem. Commun.* **1984**, 875. The maximum concentration represents a 12% yield. Given the steric congestion of the supermesitylphosphirane its photodimerization is unlikely, and formation of the diphosphene can be attributed to dimerization of supermesitylphosphinidene, a process considered but rejected by Yoshifuji (ref 18).

(25) Cowley and co-workers have demonstrated that phosphaketenes and diazidophosphines are also effective precursors for the photochemical and thermal generation of phosphinidenes: Cowley, A. H.; Gabbai, F.; Schluter, R.; Atwood, D. *J. Am. Chem. Soc.* **1992**, *114*, 3142.

Scheme IV



Scheme V



3-Methyl-1-phenyl-3-phospholene (1) and 3,4-Dimethyl-1-phenyl-3-phospholene (2).[13] To a solution of 3,4-dimethyl-1-phenyl-3-phospholene oxide (4.0 g, 19 mmol) in 5 mL of benzene was added 1.0 g (10 mmol) of phenylsilane, and the resulting mixture was heated to 70 °C and stirred for 2 h. Distillation yielded 3,4-dimethyl-1-phenyl-3-phospholene (**2**) (2.8 g, 78%), bp 95 °C (0.4 Torr): ^{31}P NMR (C_6D_6) δ −32.1 (lit.[13] −31.7); ^{1}H NMR (C_6D_6) 1.50 (br s, 6 H, Me), 2.44 (br d, 2 H, j_{gem} = 16.5 Hz, $CH_{syn}H_{anti}$), 2.71 (br dd, 2 H, J_{P-H} = 24.0 Hz, J_{gem} = 16.5 Hz, $CH_{syn}H_{anti}$), 7.10 (m, 3 H, o-, *p*-phenyl), 7.48 (m, 2 H, *m*-phenyl) (lit.[13] ($CDCl_3$) δ 1.80 (s, 6 H), 2.64 (m, 4 H), 7.56 (m, 5 H)); ^{13}C NMR (C_6D_6) δ 16.0 (Me), 40.2 (d, J_{P-C} = 11.8 Hz, CH_2), 128.54 (—Me*C*=*C*—Me), 128.55 (d, J_{P-C} = 10.2 Hz, *m*-phenyl), 130.1 (d, J_{P-C} = 3.2 Hz, *p*-phenyl), 131.6 (d, J_{P-C} = 18.9 Hz, *p*-phenyl). The same procedure was employed for the synthesis (72% yield) of 3-methyl-1-phenyl-3-phospholene (**1**): ^{31}P NMR (C_6D_6) δ −16.4 (lit.[17] (neat) −18.6); ^{1}H NMR (C_6D_6) δ 1.59 (br s, 3 H, Me), 2.29 (m, 2 H, CH_2), 2.61 (m, 2 H, CH_2), 5.25 (br s, 1 H, C=CH), 7.08 (m, 3 H, *o*-, *p*-phenyl), 7.41 (m, 2 H, *m*-phenyl), (lit.[16] (neat) 1.70 (s, 3 H, Me), 1.95–3.15 (s, 1 H, C=CH)). An inseparable impurity of 6% 3-methyl-1-phenyl-2-phospholene was detected via its ^{31}P NMR signal at δ 4.1 (lit.[17] δ 4.0).

1-Bromo-2,4,6-tri-*tert*-butylbenzene. The compound was synthesized by the method of Cowley et al.[26]

3,4-Dimethyl-1-supermesityl-3-phospholene (4). A solution of 1-bromo-2,4,6-tri-*tert*-butylbenzene (5 g, 15 mmol) in 70 mL of THF was placed in a 250-mL three-necked flask equipped with a dropping funnel, mechanical stirrer, and nitrogen inlet and cooled to −78 °C. A hexane solution of *n*-butyllithium (6.8 mL, 2.5 M, 17 mmol) was added via syringe over 5 min, and the resulting mixture was stirred for 1.5 h at −78 °C. A solution of 1-bromo-3,4-dimethyl-3-phospholene (**2**) (2.9 g, 15 mmol) in 5 mL of THF was then added from the dropping funnel. The reaction mixture was allowed to warm to room temperature and was stirred overnight. After removal of all volatile substances in vacuo, 100 mL of toluene and 25 mL of H_2O were added to the white crystalline residue under nitrogen, and the mixture was stirred for 10 min. Evaporation of solvent from the separated organic layer gave a crude product (3.2 g, 60%) that upon recrystallization from toluene at −30 °C yielded colorless crystals (2.4 g, 45%) of 3,4-dimethyl-1-supermesityl-3-phospholene (**4**), mp 128–129 °C (uncorrected): ^{13}P NMR (C_6D_6) δ 3.9; ^{1}H NMR (C_6D_6) δ 1.01 (s, 9 H, *p-t*-Bu), 1.08 (s, 6 H, 3,4-Me), 1.27 (s, 18 H, *o-t*-Bu), 2.40 (m, 4 H, CH_2), 7.10 (d, 2 H, J_{P-H} = 2.3 Hz, *m*-phenyl); ^{13}C NMR (C_6D_6) δ 15.9 (d, J_{P-C} = 3.3 Hz, 3,4-Me), 31.1 (*p*-C*Me*$_3$), 33.6 (d, J_{P-C} = 7.9 Hz, *o*-C*Me*$_3$), 33.9 (*p*-*C*Me$_3$), 39.0 (d, J_{P-C} = 2.3 Hz, *o*-*C*Me$_3$), 46.8 (d, J_{P-C} = 14.9 Hz, CH_2), 122.2 (*m*-phenyl), 129.1 (—Me*C*=*C*Me—), 144.2 (d, J_{P-C} = 47.9 Hz, *ipso*-phenyl), 146.6 (*p*-phenyl), 155.0 (d, J_{P-C} = 4.3 Hz, *o*-phenyl); UV (cyclohexane) λ_{max} = 282 nm, ϵ = 6020; MS (CI, CH_4) *m/e* (relative intensity) 358 (M^+, 16), 113 (100); exact mass determination for $C_{24}H_{39}P$ (M^+), calcd 358.2789, found 358.2786. Crystal data: monoclinic, space group $P2_{1/c}$ with a = 10.353 (2), b = 24.548 (6), and c = 10.069 (1) Å, β = 116.20 (1)°, v = 2296.1 (8) Å^3, z = 4, d_{calc} = 1.037 g cm^{-3}, μ(Mo Kα) = 1.19 cm^{-1}. A total of 4422 reflections was collected at 295 K on a Siemens R3m/V diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) and the ω scan mode. The structure was solved via direct methods and refined to a final R value of 0.0414 based on 2364 observed reflections with $I > 3\sigma(I)$. The supermesityl ring displays a nonplanar "sofa" form. Detailed discussion of this structure will be published elsewhere.

1,3,4-Trimethyl-3-phospholene (7). This compound was synthesized by the method of Quin et al.: ^{31}P NMR (C_6D_6) δ −48.8.[16]

Dichloro(mesityl)phosphine. This compound was synthesized by the method of Xie and Neilson,[27] using the procedure of Clark.[28]

Mesitylphosphine. This compound was synthesized by the method of Oshikawa and Yamashita.[29]

2,4,6-Tri-*tert*-butylphenylphosphorus Dichloride, 2,4,6-Tri-*tert*-butylphenylphosphine, and Bis(2,4,6-tri-*tert*-butylphenyl)diphosphene. These compounds were synthesized by the methods of Cowley et al.[26]

1-Mesitylphosphirane (11) and 1-(2,4,6-Tri-*tert*-butylphenyl)phosphirane (1-Supermesitylphosphirane) (12). The procedure of Oshikawa and Yamashita[20] was modified as follows: a solution of mesitylphosphine (3.0 g, 17.9 mmol) in 250 mL of THF was placed in a 500-mL flask equipped with a rubber septum and magnetic stirring bar and cooled to 0 °C. A solution of *n*-butyllithium (13.5 mL, 1.6 M, 21.6 mmol) was added dropwise with stirring. The mixture was allowed to warm to room temperature and was stirred for 30 min. Formation of monolithium mesitylphosphide was indicated by ^{31}P NMR (THF) δ −155.3 (d, $J_{P,H}$ = 168 Hz). The solution of MesPHLi was added dropwise over a 2-h period to a stirred solution of ethylene glycol ditosylate (7.4 g, 20 mmol) in 250 mL of THF cooled to −5 to 0 °C in a 1000-mL flask. When addition was complete the reaction mixture was allowed to warm to room temperature. After a further 5 h, monitoring by NMR indicated the formation of $MesPHCH_2CH_2OTs$: ^{31}P NMR (THF) δ −100.9 (d, J_{P-H} = 222 Hz). The reaction mixture was again cooled to −5 to 0 °C, and another equivalent of *n*-BuLi (14 mL, 1.6 M, 22.4 mmol) was added dropwise over 1 h. After addition was complete, the reaction mixture was allowed to warm to room temperature. After a further 10 h, monitoring the disappearance of $MesPLiCH_2CH_2OTs$ and the appearance of the phosphirane product by ^{31}P NMR indicated that the reaction was complete. Solvent was removed in vacuo, and the remaining material was mixed with 300 mL of hexane and filtered to remove lithium tosylate. After evaporation of the hexane from the filtrate, the residue was chromatographed on silica gel with hexane eluent, yielding 1-mesitylphosphirane (**11**) (1.9 g, 60%) as a colorless oil: ^{31}P NMR (C_6D_6) δ −240.8; ^{1}H NMR (C_6D_6) δ 0.94 (m, 2 H, $-CH_2CH_2-$), 1.07–1.14 (m, 2 H, $-CH_2CH_2-$), 2.06 (s, 3 H, *p*-Me), 2.43 (s, 6 H, *o*-Me), 6.64 (s, 2 H, *m*-phenyl); ^{13}C NMR ($CDCl_3$) δ 12.2 (d, J_{P-C} = 39.1 Hz, CH_2), 20.9 (*p*-Me), 22.3 (d, J_{P-C} = 8.9 Hz, *o*-Me), 128.3 (*m*-phenyl), 135.9 (d, J_{P-C} = 39.7 Hz, *ipso*-phenyl), 137.3 (*p*-phenyl), 142.2 (d, J_{P-C} = 9.6 Hz, *o*-phenyl); MS (CI, CH_4) *m/e* (relative intensity) 178 (M^+, 40), 150 (100), 135 (65), 106 (55), 105 (51); exact mass determination for $C_{11}H_{15}P$ (M^+), calcd 178.0911, found 178.0911.[30] The same procedure was followed for the synthesis of 1-(2,4,6-tri-*tert*-butylphenyl)phosphirane (**12**). The white solid product (ca. 20% yield) was purified either by silica gel column chromatography with hexane eluent or by preparative gas chromatography on a 5 × 1/4 in. o.d. aluminum column with a packing consisting of 5% SE-30 on 60/80 mesh Chromosorb W operated at 180 °C: ^{31}P NMR (C_6D_6), δ −215.7; ^{1}H NMR (C_6D_6) δ 0.90–0.96 (m, 4 H, CH_2), 1.25 (s, 9 H, *p-t*-Bu), 1.60 (s, 18 H, *o-t*-Bu), 7.36 (d, 2 H, J_{P-H} = 2.0 Hz, *m*-phenyl) (lit.[20] ($CDCl_3$) δ 1.0–1.6 (br s, 4 H, CH_2), 1.16 (s, 9 H, *p-t*-Bu), 1.40 (s, 18 H, *o-t*-Bu), 7.04 (d, 2 H, J_{P-H} = 3.9 Hz)); ^{13}C NMR (C_6D_6) δ 14.9 (d, J_{P-C} = 40.6 Hz, CH_2), 31.0 (*p*-*Me*$_3$C), 33.8 (d, J_{P-C} = 8.6 Hz, *o*-*Me*$_3$C), 34.3 (*p*-Me$_3$*C*), 38.9 (*o*-Me$_3$*C*), 122.6 (*m*-phenyl), 139.8 (d, J_{P-C} = 58.9 Hz, *ipso*-phenyl), 148.3 (*p*-phenyl), 156.4 (d, J_{P-C} = 5.1 Hz, *o*-phenyl); MS (CI, CH_4) *m/e* (relative intensity) 305 (M^+ + 1, 18), 304 (M^+, 1.2), 277 (16), 276 (16), 57 (100).

1-Mesityl-3,4-dimethyl-3-phospholene (3). 2-Bromomesitylene (3.2 g, 16 mmol) and 40 mL of THF were placed in a 150-mL Schlenk flask equipped with a rubber septum and magnetic stirring bar. While this

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mixture was stirred under argon at −78 °C, a hexane solution of *n*-BuLi (11.3 mL, 1.6 M, 18 mmol) was added via a syringe over a few-minute period. After 1 h of stirring, 1-bromo-3,4-dimethylphospholene (3 g, 16 mmol) in 30 mL of THF was added dropwise. After addition was complete the reaction mixture was allowed to warm to room temperature. After 2 h, monitoring the disappearance of the 1-bromophospholene and the appearance of the mesitylphospholene product by ^{31}P NMR indicated that reaction was complete. Solvent was removed in vacuo, and the residue was mixed with 50 mL of hexane and filtered to remove LiBr. After evaporation of the hexane from the filtrate, the residue was chromatographed on silica gel with 95% hexane–5% CH_2Cl_2 eluent, yielding white solid 1-mesityl-3,4-dimethyl-3-phospholene (**3**) (3.0 g, 81%): ^{31}P NMR (C_6D_6) δ −47.6; ^{1}H NMR (C_6D_6) δ 1.50 (s, 6 H, 3,4-Me), 2.10 (s, 3 H, *p*-Me), 2.50 (s, 6 H, *o*-Me), 2.76 (m, 4 H, CH_2), 6.77 (s, 2 H, *m*-phenyl); ^{13}C NMR (C_6D_6) δ 16.5 (d, J_{P-C} = 2.9 Hz, 3,4-Me), 20.9 (*p*-Me), 22.5 (d, J_{P-C} = 18.0 Hz, *o*-Me), 38.1 (d, J_{P-C} = 11.7 Hz, CH_2), 130.0 (d, J_{P-C} = 3.4 Hz, *m*-phenyl), 130.6 (—Me*C*=*C*Me—), 133.8 (d, J_{P-C} = 29.7 Hz, *ipso*-phenyl), 138.3 (d, J_{P-C} = 1.1 Hz, *p*-phenyl), 144.2 (d, J_{P-C} = 14.1 Hz, *o*-phenyl); MS *m/e* (CI, CH_4) (relative intensity) 232 (M^+, 11), 113 (100); exact mass determination for $C_{15}H_{21}P$ (M^+), calcd 232.1381, found 232.1399.

Photolysis of 3,4-Dimethyl-1-phenyl-3-phospholene (2). In a typical experiment a solution of 3,4-dimethyl-1-phenyl-3-phospholene (**2**) (100 mg, 0.525 mmol) and 1,3,4-trimethyl-1,3-phospholene internal standard (130 mg, 1.02 mmol) in 0.75 mL of cyclohexane was placed in a quartz photolysis tube equipped with a Teflon-brand stopcock under a nitrogen atmosphere in a drybox. The mixture was irradiated for 14 h with a bank of low-pressure mercury lamps in a Rayonet RS photochemical reactor. Conversion was 36%, and the products were *trans*- and *cis*-4,5-dimethyl-1,2-diphenyl-1,2-diphosphacyclohex-4-ene (**5** (78%) and **6** (9%)) and 2,3-dimethylbutadiene. Identification of **5** was via comparison of its ^{31}P NMR spectrum with the literature value. The structure of **6** was inferred from comparison of its NMR spectra with those of **5** and the conversion of **6** into **5** upon standing or further irradiation. **5**: ^{31}P NMR (C_6D_6) δ −23.0 (lit.[14,15] δ −23.0); ^{1}H NMR (C_6D_6) δ 1.42 (s, 6 H, Me), 2.38 (m, 4 H, CH_2), 7.08, (m, 6 H, *o*-, *p*-phenyl), 7.62 (m, 4 H, *m*-phenyl). **6**: ^{31}P NMR (C_6D_6) δ −57.8. After removal of solvent in vacuo at 95 °C, the only product was **5**.

Irradiation of 1,3,4-Trimethyl-3-phospholene (7). Solutions of 1,3,5-trimethyl-3-phospholene (**7**) (30 mg, 0.23 mmol) in 150 μL of cyclohexane and C_6D_6 in degassed quartz tubes were irradiated for 24 h at 254 nm in the Rayonet reactor. Both the ^{31}P and the ^{1}H NMR spectra were unchanged.

Photolysis of 3-Methyl-1-phenyl-3-phospholene (1) in the Presence of 2,3-Dimethylbutadiene. In a typical experiment a mixture of 3-methyl-1-phenyl-3-phospholene (**1**) (100 mg, 0.57 mmol), 1,3,4-trimethyl-3-phospholene (**7**) internal standard (59 mg, 0.46 mmol), and 2,3-dimethylbutadiene (48 mg, 0.57 mmol) in 7 mL of cyclohexane was placed into the quartz photolysis tube under nitrogen in a drybox. The ^{31}P NMR spectrum was recorded. After freeze–pump–thaw degassing on a vacuum line to 0.02 Torr, the reaction mixture was irradiated at 254 nm in the Rayonet reactor for 13 h. From the ^{31}P NMR spectrum the conversion (31%) and yields of the products 3,4-dimethyl-1-phenyl-3-phospholene (**2**) (13%), *trans*- and *cis*-4,5-dimethyl-1,2-diphenyl-1,2-diphosphacyclohex-4-ene (**5** and **6**) (26% and 17%, respectively) were determined.

Procedures for Photolysis of 3,4-Dimethyl-1-supermesityl-3-phospholene (4), 1-Mesitylphosphirane (11), and 1-Supermesitylphosphirane (12). Cyclohexane or C_6D_6 solutions of the reactants (typically 0.07–0.017 mmol in 0.7 mL) were loaded into a quartz NMR tube in the drybox under nitrogen or argon, and the tube was sealed with a rubber septum. The reaction mixtures, housed in a quartz water jacket to keep the reaction temperature between 15 and 20 °C, were irradiated at 254 nm with an array of low-pressure mercury lamps in the Rayonet reactor. Conversions of 16–55% were obtained with irradiations of 2–16 h. When possible, products were isolated by preparative gas chromatography or column chromatography on silica gel with hexane eluent, as indicated. 1-Mesityl-3,4-dimethyl-3-phospholene (**3**) was isolated by GC and identified by comparison with an authentic sample described above. 3,3-Dimethyl-5,7-di-*tert*-butylphosphaindan (**8**): ^{31}P NMR (C_6D_6) δ −79.5 (d, J_{H-P} = 173.4 Hz) (lit.[18] ($CDCl_3$) δ −79.6 (d, J_{H-P} = 173.3 Hz)). Permesitylcyclotriphosphine (**13**): ^{31}P NMR (C_6D_6) (A_2B system) δ −109.8 (d, J_{B-A} = 184.9 Hz, P_A), −143.9 (t, J_{A-B} = 184.9 Hz, P_B) (lit.[15] −111.6 (d, J_{B-A} = 179 Hz, P_A), −145.8 (t, J_{A-B} = 179 Hz, P_B)). Permesitylcyclotetraphosphine (**14**): ^{31}P NMR (C_6D_6) δ −43.2 (lit.[15] −45.4). Vinyl(mesityl)phosphine (unstable) (**15**): ^{31}P NMR (C_6D_6) δ −80.9 (ddt, $J_{H\alpha-P}$ = 220.1 Hz, $J_{H\beta-P}$ = 12.2 Hz, $J_{H\gamma-P}$ = 23 Hz) (lit.[31] for MesPHCMe=CH_2 δ −74 ($J_{H\alpha-P}$ = 222 Hz)). 2-Isopropenyl-1-mesityl-2-methylphosphirane (**16**) (unstable and could not be isolated): ^{31}P NMR (C_6D_6) δ −175.7. 1-Mesityl-2,3-diethylphosphirene (**18**) (isolated by GC and column chromatography): ^{31}P (C_6D_6) δ −181.9; ^{1}H NMR (C_6D_6) δ 1.02 (t, 6 H, J_{H-H} = 7.4 Hz, CH_2CH_3), 2.10 (s, 3 H, *p*-Me), 2.42 (m, 4 H, CH_2), 2.56 (s, 6 H, *o*-Me), 6.69 (s, 2 H, *m*-phenyl); ^{13}C NMR (C_6D_6) δ 12.2 (CH_2CH_3), 20.6 (*p*-Me), 20.9 (d, J_{P-C} = 8.9 Hz, *o*-Me), 21.5 (d, J_{P-C} = 9.4 Hz, CH_2), 128.2 (d, J_{P-C} = 47.3 Hz, C=C), 128.8 (*m*-phenyl), 136.5 (*p*-phenyl), 140.8 (d, J_{P-C} = 9.6 Hz, *o*-phenyl), 142.4 (d, J_{P-C} = 77 Hz, *ipso*-phenyl); MS (CI, CH_4) *m/e* (relative intensity) 232 (M^+, 13), 113 (100); exact mass determination for $C_{15}H_{21}P$ (M^+), calcd 232.1381, found 232.1380. 7-Mesityl-7-phosphanorcarane (**19**) (isolated by column chromatography): ^{31}P NMR spectroscopy of the reaction mixture revealed the formation of two products at δ −203.5 and −202.8. Only one product was found upon silica gel chromatography under a nitrogen atmosphere (hexane eluent), to which the structure *anti*-7-mesityl-7-phosphanorcarane was assigned: ^{31}P NMR (C_6D_6) δ −203.5; ^{1}H NMR (C_6D_6) δ 1.40 (m, 10 H, cyclohexyl), 2.08 (s, 3 H, *p*-Me), 2.47 (s, 6 H, *o*-Me), 6.68 (s, 2 H, *m*-phenyl); IR (GCIR) ν (cm^{-1}) 1430, 1570, 2820, 2930, 3020; MS *m/e* (relative intensity) 232 (M^+, 30), 150 (100); exact mass determination for $C_{15}H_{21}P$ (M^+), calcd 232.1381, found 232.1377.

Pyrolysis of 1-Mesitylphosphirane (11) in the Presence of 2,3-Dimethylbutadiene. 1-Mesitylphosphirane (**11**) (20 mg, 0.11 mmol), 2,3-dimethylbutadiene (164 mg, 2 mmol), and 0.2 mL of C_6D_6 were placed in a 5-mm o.d. Pyrex tube, and the mixture was degassed by freeze–pump–thaw cycling on a vacuum line at 0.02 Torr and then sealed and the ^{31}P NMR spectrum recorded. The reaction mixture was heated 80 min in a preheated oil bath at 190 °C. The tube was then frozen with liquid N_2 and opened, and the ^{31}P NMR spectrum was again recorded. The products were identified and their yields determined on the basis of the chemical shifts and intensities of their ^{31}P NMR signals. The ^{31}P NMR spectrum of 1-mesityl-3,4-dimethyl-3-phospholene (3) is reported above. The permesitylcyclopolyphosphines cyclo-$(PMes)_n$ (n = 3, 4) **13** and **14** were identified by comparison with the literature data cited above.[14,15] Dimesitylphosphine was isolated by gas chromatography and identified by comparison of its spectra with published values: ^{31}P NMR (C_6D_6) δ −92.5 (d, J_{H-P} = 230.0 Hz) (lit.[32] (Et_2O) δ 92.4, J_{H-P} = 235 Hz); ^{1}H NMR (C_6D_6) δ 2.06 (s, 6 H, *p*-Me), 2.26 (s, 12 H, *o*-Me), 5.30 (d, 1 H, J_{P-H} = 230.0 Hz PH), 6.69 (s, 4 H, *m*-phenyl), (lit.[32] ($CDCl_3$) δ 2.28 (s, 9 H), 5.36 (d, J_{P-H} = 235 Hz), 6.87 (s, 2 H)); ^{13}C NMR (C_6D_6) δ 20.6 (*p*-Me), 22.5 (d, J_{P-C} = 11.2 Hz, *o*-Me), 129.5 (d, J_{P-C} = 2.5 Hz, *m*-phenyl), 137.8 (*p*-phenyl), 142.4 (d, J_{P-C} = 12.5 Hz, *o*-phenyl). The previously unreported structure 1,2-dimesityl-4,5-dimethyl-1,2-diphosphacyclohex-4-ene (**17**) was assigned to a product that was unstable and could not be purified. The characterization was based on its ^{31}P signal (C_6D_6) δ −58.3, which is similar to the chemical shift δ −57.8 of the compound assigned the structure *cis*-4,5-dimethyl-1,2-diphenyl-1,2-diphosphacyclohex-4-ene (**6**) above.

Photolysis of 1-Supermesitylphosphirane (12) Monitored by Ultraviolet Spectroscopy. A solution of 1-supermesitylphosphirane (**12**) in cyclohexane (0.7 mL, 2.74 × 10^{-3} M) was placed in a quartz NMR tube under an inert atmosphere in a drybox and sealed with a rubber septum. Ultraviolet irradiation at 254 nm with a bank of low-pressure mercury lamps in a Rayonet reactor was interrupted to record UV spectra (employing a pure cyclohexane blank). Concentrations of 1,2-bis(supermesityl)diphosphene (**9**), UV (C_6H_{12}) λ_{max} = 345 nm, ϵ = 6780 (lit.[33] (CH_2Cl_2) λ_{max} = 340 nm, ϵ = 7690), were calculated from absorption peak intensities: 5 min, 1.5 × 10^{-5} M; 10 min, 7.5 × 10^{-5} M; 15 min, 1.4 × 10^{-4} M; 30 min, 1.8 × 10^{-4} M; 60 min, 1.7 × 10^{-4} M. The experiment was also performed on a 4.8 × 10^{-2} M solution, employing the same solution as the blank, and the absorption maximum corresponding to 1,2-bis(supermesityl)diphosphene was observed to shift as follows: 5 min, 320 nm; 10 min, 335 nm; 15 min, 345 nm; 20 min, 355 nm; 50 min, 358 nm. The formation of the *trans*-diphosphene was confirmed at the end of the experiment by observation of the ^{31}P NMR signal at δ 495 (lit.[18] δ 488.5).

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Supplementary Material Available: Structure determination summary, tables of atomic coordinates, bond lengths, bond angles, and anisotropic displacement coefficients, and a molecular diagram (8 pages); observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

σ-Hydrocarbyl-Bridged Gallium/Zirconium Complexes Containing Planar-Tetracoordinate Carbon

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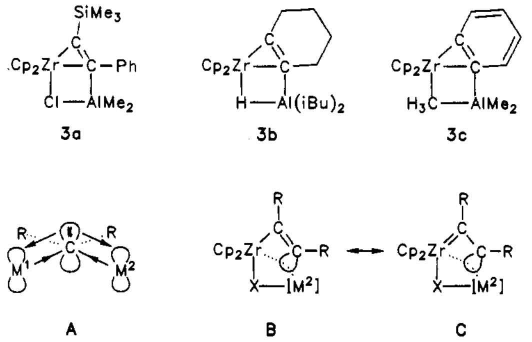
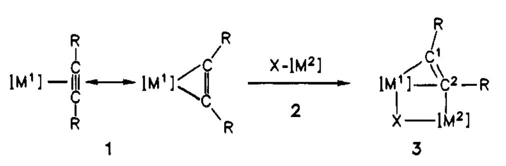
Abstract: Several examples are described where in situ generated (η^2-alkyne) group 4 metallocene type substrates add to X-[M^2] reagents (M^2 = main group metal) to form dimetallabicyclic products $Cp_2M(\mu\text{-}\eta^1{:}\eta^2\text{-}RCCR)(\mu\text{-}X)[M^2]$ which contain a planar-tetracoordinate carbon center in the $\mu\text{-}\eta^1{:}\eta^2$-hydrocarbyl bridge. Thus, (η^2-cyclohexyne)(PMe_3)$ZrCp_2$ (**4a**) reacts in this way with excess trimethylgallium to give $Cp_2Zr(\mu\text{-}\eta^1{:}\eta^2\text{-}C_6H_8)(\mu\text{-}CH_3)GaMe_2$ (**6a**). Complex **6a** is one of the rare examples of a gallium compound containing σ-hydrocarbyl bridges to this heavy main group metal. Complex **6a** was characterized by X-ray diffraction. It crystallizes in space group $P2_1/c$ with cell parameters a = 9.007 (3) Å, b = 8.195 (2) Å, c = 25.404 (4) Å, β = 91.30 (1)°, Z = 4, R = 0.056, and R_w = 0.066. Complex **6a** contains a planar-tetracoordinate carbon atom C(2) with pertinent bond distances and angles of 2.423 (5) Å [Zr–C(2)], 2.096 (5) Å [Ga–C(2)], 1.572 (8) Å [C(2)–C(3)], 1.314 (7) Å [C(1)–C(2)], 119.5 (4)° [C(3)–C(2)–C(1)], 100.3 (3)° [C(3)–C(2)–Ga], 79.3 (1)° [Ga–C(2)–Zr], and 61.1 (3)° [C(1)–C(2)–Zr]. Both Cp rings are disordered. Zirconium and gallium seem to form a three-center two-electron bond with C(2). The planar-tetracoordinate geometry at carbon atom C(2) is probably electronically stabilized by the σ-donor properties of the attached metal centers and by a π-conjugative interaction of the C(2)–C(1)–Zr moiety normal to the σ-plane. (η^2-1,2-Didehydrobenzene)(PMe_3)$ZrCp_2$ (**4b**) reacts analogously with trimethylgallium to give $Cp_2Zr(\mu\text{-}\eta^1{:}\eta^2\text{-}C_6H_4)(\mu\text{-}CH_3)GaMe_2$ (**6b**) in almost quantitative yield. Complex **6b** crystallizes isomorphously to the corresponding Al compound in space group $P2_1/n$ with cell parameters a = 9.126 (1) Å, b = 14.080 (2) Å, c = 14.323 (1) Å, β = 103.88 (1)°, Z = 4, R = 0.062, and R_w = 0.038. It also contains a planar-tetracoordinate carbon atom [C(2)]. The reaction of Ph—C≡C—$GaMe_2$ (**7**) with (hydrido)zirconocene chloride produces $Cp_2Zr(\mu\text{-}PhCCH)(\mu\text{-}Cl)GaMe_2$ (**9**) which is probably also a similarly structured "anti-van't Hoff/LeBel complex". Complexes **6a** and **6b** react with ethylene or norbornene at room temperature with liberation of Me_3Ga and formation of five-membered metallacyclic products (e.g., bis(η-cyclopentadienyl)zirconaindane is obtained from **6b** and ethylene).

Dimetallic complexes containing the main group metal gallium combined with a variety of d-block elements are rather abundant although it is noticeable that they always seem to contain metal–metal bonds and apparently never μ-hydrocarbyl bridges to connect the metal centers.[1] In this respect the group 3 element gallium seems to behave strikingly different from its lighter homologue aluminum from which numerous examples of σ-hydrocarbyl-bridged complexes are known.[2] The observed structural differences of the respective homoleptic R_3M species may serve to illustrate this point: trimethylgallium has shown to be a monomer in solution as well as in the gas-phase,[3] whereas the $Me_2Al(\mu\text{-}CH_3)_2AlMe_2$ trimethylaluminum dimer is favored by some 20 kcal mol^{-1} over its dissociated monometallic building blocks.[4] Gallium even seems to disfavour π-bridging to some extent. In contrast to the strong Al–C(Ar) linkages in the stable ($R_2Al\text{-}C_6H_5$) dimers,[5] the aryl–carbon to gallium π-interaction in, e.g., $(phenyl)_3Ga$ associates in the solid state seems to be rather weak.[6,7]

Scheme I



We have recently found an unprecedentedly simple way of synthesizing heterodimetallic hydrocarbyl-bridged zirconium (or hafnium)/aluminum compounds (**3**) that contain a planar-tetracoordinate carbon in the bridge. The essential step of the reaction sequence consists of the addition of the main group metal component X-[M^2] (**2**) to a very reactive (η^2-alkyne)transition metal reagent (**1**) which is usually generated in situ from an appropriate precursor in the course of the reaction.[8]



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(1) Compton, N. A.; Errington, R. J.; Norman, N. C. *Adv. Organomet. Chem.* **1990**, *31*, 91. Fischer, R. A.; Behm, J. *Chem. Ber.* **1992**, *125*, 37.

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