

(0.27 mL, 2.41 mmol). The mixture was stirred at 0 °C for 30 min during which time the pale yellow solution became deep red. GC analysis of the solution showed the disappearance of the alkyne and the formation of 2 equiv of styrene. Addition of ethanol and concentration of the solvent afforded cherry-red microcrystals of **6**, yield 65%. IR:  $\nu(\text{C}\equiv\text{C})$  2062  $\text{cm}^{-1}$  (m); phenyl reinforced vibration 1590  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{78}\text{H}_{75}\text{BOP}_4\text{Ru}$ : C, 74.11; H, 5.98; Ru, 7.99. Found: C, 74.09; H, 5.80; Ru, 7.86.  $^{31}\text{P}\{^1\text{H}\}$  NMR (121.42 MHz, acetone- $d_6$ , -60 °C,  $\text{H}_3\text{PO}_4$  85% reference):  $\text{AM}_2\text{Q}$  system,  $\delta(\text{P}_A)$  153.74,  $\delta(\text{P}_M)$  50.24,  $\delta(\text{P}_Q)$  47.38;  $J(\text{P}_A\text{P}_M)$  5.2 Hz,  $J(\text{P}_A\text{P}_Q)$  3.1 Hz,  $J(\text{P}_M\text{P}_Q)$  21.7 Hz.

**Attempted Synthesis of  $[(\text{PP}_3)\text{Ru}(\text{C}(\text{H})=\text{C}(\text{H})\text{Ph})]^+$  (**7**).** When the above reaction was performed by reacting **2** with 2.5 equiv of phenylacetylene, a ca. 1:1 mixture of the starting complex **2** and of the alkynyl complex **6** was obtained. However, variable-temperature  $^{31}\text{P}$  NMR analysis of the reaction mixture in acetone- $d_6$  provides evidence for the formation of an intermediate species **7** which initially forms at the expense of **2** and then rapidly converts to **6**.  $^{31}\text{P}\{^1\text{H}\}$  NMR (121.42 MHz, acetone- $d_6$ , -60 °C,  $\text{H}_3\text{PO}_4$  85% reference):  $\text{AM}_2\text{Q}$  system,  $\delta(\text{P}_A)$  152.46,  $\delta(\text{P}_M)$  46.39,  $\delta(\text{P}_Q)$  51.82;  $J(\text{P}_A\text{P}_M)$  2.8 Hz,  $J(\text{P}_A\text{P}_Q)$  2.8 Hz,  $J(\text{P}_M\text{P}_Q)$  21.9 Hz.

**Reaction of **6** with  $\text{HC}\equiv\text{CPh}$ .** Neat phenylacetylene (28  $\mu\text{L}$ , 0.25 mmol) was syringed at room temperature into a THF solution (25 mL) of **6** (0.25 g, 0.21 mmol). The solution was stirred under nitrogen for 15 min, during which time the starting red color turns light yellow.  $^{31}\text{P}\{^1\text{H}\}$  NMR analysis of the reaction mixture shows the quantitative formation of **3a,b**.

**Reaction of **6** with  $\text{H}_2$ .** A THF solution (25 mL) of **6** (0.25 g, 0.21 mmol) under hydrogen (1 atm) was heated at 60 °C for 30 min, during which time the color changed gradually from red to yellow. By addition of ethanol (30 mL) and partial evaporation of the solvent under a stream of nitrogen, yellow crystals of **2** precipitated in 90% yield. GC analysis of the reaction mixture

showed the formation of 1 equiv of styrene.

**Catalytic Hydrogenation Reactions. Low-Pressure Experiments.** The catalytic reactions were followed by measuring the hydrogen consumption as a function of time on a gas buret (Afora 516256). Analysis of the products of the catalytic reactions was carried out on a Perkin-Elmer 8500 gas chromatograph with an FFAP on Chromosorb GHP 80/100 mesh ( $3.6 \times 1/8$  in.) column at 160 °C.

The catalyst precursors **2** and **3a,b** were carried with a degassed solution of the substrate in 1,2-dichloroethane (8 mL) into a Schlenk manifold. The flask was closed by a silicone septum. The system was evacuated and refilled with hydrogen six times, and the flask was then immersed in a constant-temperature bath. The mixture was vigorously shaken during the run. Plots of the kinetic data were fitted by use of conventional linear regression programs.

**High-Pressure Experiments.** Air was evacuated from the autoclave; then, the solution containing the catalyst, the substrate, and the solvent, prepared in a Schlenk tube, was introduced by suction. Hydrogen was added up to the desired pressure, and the solution in the autoclave was stirred at the selected temperature. At the end of the reaction, the autoclave was cooled, the gas was vented out, and the solution was collected. The conversion was determined from the crude product by GC analysis with a 2-m packed column containing a fatty acid phase (5%) on Chromosorb G AW-DMCS.

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## Synthesis and Structure of (Phosphaalkenyl)mercury Compounds

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The (phosphaalkenyl)mercury compounds (*E*)-Mes\*P=CHHgCl [(*E*)-**4**], (*Z*)-Mes\*P=CHHgCl [(*Z*)-**4**], (*E,E*)-(Mes\*P=CH)<sub>2</sub>Hg [(*E,E*)-**5**], and (*Z,Z*)-(Mes\*P=CH)<sub>2</sub>Hg [(*Z,Z*)-**5**] (Mes\* = 2,4,6-tri-*tert*-butylphenyl) were prepared from (*E/Z*)-Mes\*P=CHLi [(*E/Z*)-**3**] or (*Z*)-Mes\*P=CHLi [(*Z*)-**3**], respectively, and HgCl<sub>2</sub>. The *Z* isomers (*Z*)-**4** and (*Z,Z*)-**5** were more stable than the corresponding *E* isomers: (*E,E*)-**5** decomposed and (*E*)-**4** and (*E,E*)-**5** rearranged to the corresponding *Z* isomers. The X-ray crystal structure determination of (*Z,Z*)-**5** was carried out; crystals are monoclinic, space group  $P2_1/c$  with unit-cell dimensions  $a = 13.8800$  (7),  $b = 14.4938$  (6),  $c = 19.8504$  (5) Å, and  $\beta = 104.494$  (3)°, final  $R = 0.0497$ , and  $R_w = 0.0313$  for 2671 reflections with  $I > 2.5\sigma(I)$  and 375 parameters. The results show a double *Z* configuration with the mercury atom sandwiched between the two phenyl rings; the phenyl rings are slightly bent toward the mercury atom, indicating a stabilizing interaction between these groups. When (*Z,Z*)-**5** was reacted with *n*-butyllithium, only lithium-mercury exchange was observed.

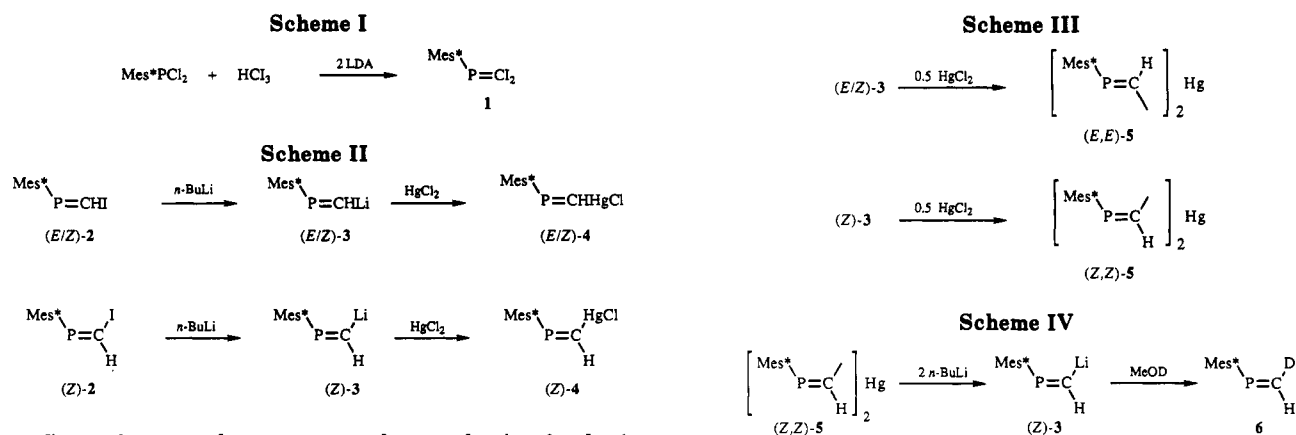
### Introduction

Phosphaalkenes  $\text{RP}=\text{CXY}$  containing a phosphorus-carbon double bond—and therefore not so long ago believed to be incapable of existence<sup>1</sup>—have in recent years

become increasingly known to be stable compounds if properly substituted.<sup>2</sup> Still, several goals wait to be accomplished: one concerns the stereochemistry around the  $\text{P}=\text{C}$  bond, i.e., a convenient way to determine the *E/Z*

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configuration; another concerns the synthesis of substituted phosphalkenes, i.e., the desirability to widen the range of functionalities at X and Y and to make their introduction easier and more general.

In pursuit of the synthetic goal, we<sup>3</sup> and others<sup>4</sup> have recently started to investigate the potential of C-halogenated phosphalkenes and of C-metal derivatives derived from them to prepare new functionalized phosphalkenes.

As more of such phosphalkenes became available, the stereochemical problems became increasingly obnoxious. Obviously, an X-ray crystal structure determination is the safest way to define the configuration around the P=C double bond; however, it is laborious and depends on the availability of suitable crystals. A more convenient method would be NMR spectroscopy, and indeed, a more or less empirical rule, the so-called "cis rule", has been proposed which states that nuclei in substituent X have a larger coupling to phosphorus, if they are cis relative to the phosphorus lone pair. The cis rule had first been derived for normal, tricoordinated phosphines<sup>5</sup> and placed on a theoretical foundation.<sup>5,6</sup> Furthermore, it holds not only for nuclei directly bonded to the  $\alpha$ -carbon, but also for more remote positions. In the course of our investigations on phosphalkenes,<sup>3</sup> we had to further specify this rule in such a way that it is applicable only to the more positive of the substituents X or Y; for the other one, the reverse was found; i.e., the nuclei cis to the lone pair had the smaller coupling.

The present investigations in the *P*-supermesityl series (supermesityl = Mes\* = 2,4,6-tri-*tert*-butylphenyl) were undertaken both to increase the range of metals in phosphalkenes by mercury and to furnish additional support for the validity of the cis rule.

### Synthesis

Starting materials for the organomercury compounds to be described were the C-iodophosphalkenes Mes\*P=Cl<sub>2</sub> (1) and Mes\*P=CHI (2). The latter are available as an *E/Z* mixture ((*E,Z*)-2 in a ratio of 80:20) or as the pure *Z* isomer ((*Z*)-2).<sup>3</sup> Compound 1 has previously been ob-

tained by different routes.<sup>3,4,d,i</sup> We found that it can most conveniently be prepared by the reaction of Mes\*PCl<sub>2</sub> and iodoform with 2 equiv of lithium diisopropylamide (LDA) at low temperatures (Scheme I).

Compounds 2 undergo a halogen-metal exchange reaction with *n*-butyllithium at -80 °C to form the (phosphaalkenyl)lithium reagents (*E/Z*)-3 and (*Z*)-3, respectively.<sup>3,4c</sup> Reaction of 3 with 1 equiv of HgCl<sub>2</sub> furnishes 4 (Scheme II). The ratio of (*E,Z*)-4 in the unpurified reaction mixture was analogous to that in the starting material (*E/Z*)-2, namely 80:20. However, when this (*E,Z*)-4 mixture was worked up by evaporation followed by extraction with toluene, only (*Z*)-4 was isolated in 31% yield; note that this yield is higher than expected from the 20% of (*Z*)-2 originally present in the starting material.

When only 0.5 equiv of HgCl<sub>2</sub> was added to 3, compounds (*E,E*)-5 and (*Z,Z*)-5 were formed (Scheme III). From (*E,Z*)-2, one would expect a mixture of (*E,E*)-5, (*E,Z*)-5, and (*Z,Z*)-5 in a ratio of 64:32:4. However, only (*E,E*)-5 and (*Z,Z*)-5 were observed in the <sup>31</sup>P NMR spectrum of the unpurified reaction mixture in a ratio of 80:20.

Compounds (*E,E*)-5 and (*Z,Z*)-5 could be purified by crystallization from pentane. Again, when pure (*E,E*)-5, as obtained after the first crystallization, was further crystallized in an attempt to obtain crystals suitable for structure determination, only (*Z,Z*)-5 was isolated in low yield; the mother liquor contained mainly Mes\*P=CH<sub>2</sub>. In contrast, (*Z,Z*)-5 crystallized as beautiful single crystals and was completely stable toward moisture, even in solution. It was not possible to measure the NMR spectra of (*E,E*)-5 in C<sub>6</sub>D<sub>6</sub>, because it decomposed too rapidly; a small amount of (*Z,Z*)-5 was detected by <sup>31</sup>P NMR spectroscopy. In CDCl<sub>3</sub> solution, however, decomposition and isomerization were slow and could not be observed during the NMR measurements (about 1 day). Apparently, the *E* isomers (*E*)-4, (*E,E*)-5, and presumably (*E,Z*)-5 tend to rearrange the *Z* isomers and/or decompose. *E/Z* isomerizations of phosphalkenes are known,<sup>7</sup> but systematic investigations have not been reported and the mechanistic

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**Table I. Final Coordinates and Equivalent Isotropic Thermal Parameters for the Non-Hydrogen Atoms of (Z,Z)-5<sup>a</sup>**

atom	x	y	z	U(eq), <sup>b</sup> Å <sup>2</sup>
Molecule 1				
Hg(11)	0	1/2	0	0.0554 (4)
P(101)	0.2189 (3)	0.3954 (3)	0.03586 (19)	0.0522 (17)
C(101)	0.1472 (8)	0.4812 (7)	0.0474 (5)	0.056 (5)
C(102)	0.1294 (7)	0.3243 (6)	-0.0294 (5)	0.035 (4)
C(103)	0.1054 (7)	0.3486 (6)	-0.1026 (6)	0.029 (4)
C(104)	0.1702 (8)	0.4131 (7)	-0.1368 (6)	0.043 (4)
C(105)	0.2800 (8)	0.4067 (8)	-0.1027 (6)	0.071 (6)
C(106)	0.1585 (8)	0.3840 (7)	-0.2127 (5)	0.063 (5)
C(107)	0.1353 (8)	0.5137 (8)	-0.1365 (5)	0.074 (5)
C(108)	0.0201 (8)	0.3143 (6)	-0.1449 (5)	0.035 (4)
C(109)	-0.0429 (8)	0.2543 (8)	-0.1233 (6)	0.038 (5)
C(110)	-0.1397 (8)	0.2210 (7)	-0.1715 (6)	0.044 (4)
C(111)	-0.2226 (8)	0.2621 (10)	-0.1504 (7)	0.158 (10)
C(112)	-0.1499 (8)	0.1186 (8)	-0.1678 (6)	0.104 (7)
C(113)	-0.1496 (9)	0.2438 (10)	-0.2458 (6)	0.142 (9)
C(114)	-0.0153 (8)	0.2259 (7)	-0.0558 (5)	0.035 (4)
C(115)	0.0711 (8)	0.2543 (7)	-0.0081 (6)	0.035 (4)
C(116)	0.0956 (12)	0.2099 (10)	0.0668 (7)	0.056 (6)
C(117)	0.0407 (10)	0.2631 (9)	0.1128 (6)	0.097 (9)
C(118)	0.0579 (9)	0.1110 (8)	0.0619 (6)	0.099 (7)
C(119)	0.2044 (9)	0.2050 (9)	0.1007 (6)	0.111 (8)
Molecule 2				
Hg(21)	1/2	0	0	0.0729 (5)
P(201)	0.7239 (3)	0.0901 (3)	0.0237 (2)	0.0633 (17)
C(201)	0.6306 (7)	0.0344 (7)	-0.0274 (5)	0.066 (6)
C(202)	0.6787 (7)	0.1048 (7)	0.1021 (5)	0.032 (4)
C(203)	0.6988 (8)	0.0332 (7)	0.1542 (5)	0.044 (5)
C(204)	0.7820 (10)	-0.0394 (8)	0.1640 (7)	0.065 (6)
C(205)	0.8107 (9)	-0.0793 (8)	0.2355 (6)	0.109 (8)
C(206)	0.8751 (8)	0.0001 (10)	0.1478 (6)	0.111 (7)
C(207)	0.7438 (10)	-0.1189 (8)	0.1149 (7)	0.117 (9)
C(208)	0.6428 (8)	0.0346 (7)	0.2027 (5)	0.049 (5)
C(209)	0.5690 (8)	0.0995 (8)	0.2035 (5)	0.046 (5)
C(210)	0.5032 (9)	0.0906 (9)	0.2552 (6)	0.061 (5)
C(211)	0.5606 (8)	0.0591 (9)	0.3721 (5)	0.097 (7)
C(212)	0.4553 (9)	0.1824 (8)	0.2666 (6)	0.105 (8)
C(213)	0.4186 (8)	0.0228 (10)	0.2275 (5)	0.105 (7)
C(214)	0.5593 (8)	0.1701 (7)	0.1572 (5)	0.046 (5)
C(215)	0.6153 (8)	0.1751 (8)	0.1075 (5)	0.038 (4)
C(216)	0.5979 (11)	0.2659 (10)	0.0627 (8)	0.051 (6)
C(217)	0.6918 (9)	0.2976 (7)	0.0431 (6)	0.087 (7)
C(218)	0.5692 (10)	0.3464 (7)	0.1025 (7)	0.100 (8)
C(219)	0.5120 (11)	0.2502 (9)	-0.0026 (7)	0.127 (8)

<sup>a</sup>Atomic labels of the type X(ijk), with *i* = 1, 2 referring to molecules 1 and 2, respectively. <sup>b</sup>U(eq) =  $\sum_i \sum_j U_{ij} a_i^* a_j^* (\mathbf{a}_i \cdot \mathbf{a}_j)$ .

picture is unclear. In the case of 4 and 5, the mechanisms of these processes were not established.

Attempts to prepare (E,Z)-5 in a systematic fashion failed. The reaction of (E/Z)-3 with (Z)-4 gave (according to <sup>31</sup>P NMR spectroscopy) only (Z,Z)-5 in low yield and some unidentified side products.

Like other organomercury compounds, 5 may serve as the starting material for further transformations. Thus, the reaction of (Z,Z)-5 with 2 equiv of *n*-butyllithium at -80 °C gave (Z)-3, as evidenced by MeOD quench, leading to 6<sup>3</sup> (Scheme IV). No reaction, however, took place when 2 equiv of LDA was added to (Z,Z)-5.

### Crystal Structure of (Z,Z)-5

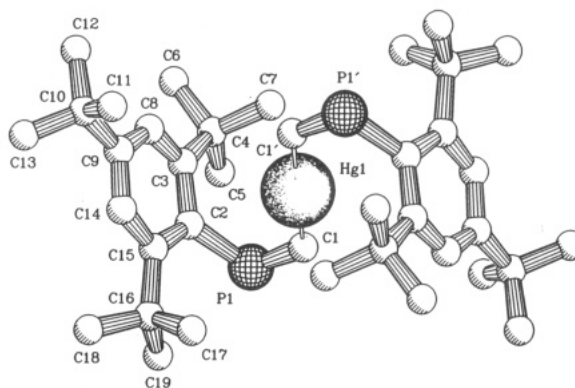
The crystal structure of (Z,Z)-5 contains two crystallographically independent molecules, which are virtually identical. The Hg atom of both molecules is located on one site; therefore, only one Mes\*PCH unit of each independent molecule is unique. Coordinates are given in Table I; selected geometrical parameters are supplied in Table II. A PLUTON drawing of one of the independent molecules, together with the adopted atom numbering scheme, is given in Figure 1.

**Table II. Selected Bond Distances (Å) and Bond Angles (deg) with Esd's in Parentheses for (Z,Z)-5**

	molecule 1	molecule 2
Hg(1)-C(1)	2.042 (11)	2.079 (10)
P(1)-C(1)	1.644 (12)	1.643 (11)
P(1)-C(2)	1.865 (10)	1.830 (11)
C(1)-Hg(1)-C(1')	180	180
C(1)-P(1)-C(2)	101.2 (5)	101.4 (5)
Hg(1)-C(1)-P(1)	127.4 (6)	124.1 (6)

**Table III. Crystal Data and Details of the Structure Determination of (Z,Z)-5**

Crystal Data	
formula	C <sub>38</sub> H <sub>60</sub> HgP <sub>2</sub>
mol wt	779.43
cryst system	monoclinic
space group	P2 <sub>1</sub> /a (No. 14)
<i>a</i> , <i>b</i> , <i>c</i> , Å	13.8800 (7), 14.4938 (6), 19.8504 (5)
$\beta$ , deg	104.494 (3)
<i>V</i> , Å <sup>3</sup>	3866.3 (3)
<i>Z</i>	4
<i>D</i> <sub>calc</sub> , g cm <sup>-3</sup>	1.339
<i>F</i> (000)	1592
$\mu$ , cm <sup>-1</sup>	40.8
cryst size, mm	0.4 × 0.5 × 0.8
Data Collection	
temp, K	298
$\theta_{\min}$ , $\theta_{\max}$ , deg	1.1, 27.5
radiation	Mo K $\alpha$ (Zr filter), 0.71073 Å
$\Delta\omega$ , deg	1.09 + 0.35 tan $\theta$
hor, vert aperture, mm	3.00, 5.00
refld reflns	-2,4,0; 2,2,-4; 2,4,2
data set	-18:18; -18:0; -25:0
total, unique data, <i>R</i> <sub>int</sub>	9476, 8857, 0.045
obsd data	2671 [ <i>I</i> > 2.5 $\sigma$ ( <i>I</i> )]
abs correctn range (DIFABS)	0.75, 1.28
Refinement	
no. of refld params	375
no. of reflns	2671
weighting scheme	1/ $\sigma^2$ ( <i>F</i> )
final <i>R</i> , <i>R</i> <sub>w</sub> , <i>S</i>	0.0497, 0.0313, 3.31
( $\Delta/\sigma$ ) <sub>av</sub> in final cycle	0.048
min, max resid dens, e Å <sup>3</sup>	-0.62, 0.72



**Figure 1.** PLUTON drawing of (Z,Z)-5 with the adopted atom labeling scheme; see also Table I. Only one independent molecule is shown. Hydrogen atoms are omitted for clarity.

The crystal structure firmly establishes the double *Z* configuration of (Z,Z)-5 (Figure 1) and thus forms a reliable basis for the assignment of NMR data (vide infra).

The mercury atom has the normal linear coordination geometry (C101-Hg1-C101' = 180 °); the Hg-C bond lengths, however, are on the short side (Hg1-C101 = 2.042 (11) Å; Hg2-C201 = 2.079 (10) Å). They can best be compared with alkenyl (vinyl) mercury compounds like (E,E)-(HPHC=CH)<sub>2</sub>Hg; this compound has a C-Hg bond length of 2.07 Å.<sup>8</sup> The C-Hg bond lengths of *trans*-

Table IV. Characteristic NMR Data for 4 and 5

compound	$\delta(^1\text{H})^a$ (P=CH)	$\delta(^{13}\text{C})^a$ (P=C)	$\delta(^{31}\text{P})^a$	$\delta(^{199}\text{Hg})^a$	$^2J(\text{PH})^b$	$^2J(\text{P}^{199}\text{Hg})^b$	$^1J(\text{P}=\text{C})^b$	$^3J(\text{PC})^b$
(E)-4 <sup>c</sup>			311		27	1365		
(Z)-4	7.96	183.0	333.6	-1152	30	368	55	
(E,E)-5	8.45	203.3	315.8	-600	24	805	75	7.2
(Z,Z)-5	8.15	208.6	343.4	-818	28	182	54	4.2

<sup>a</sup> Parts per million, relative to TMS (<sup>13</sup>C, <sup>1</sup>H), 85% H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P), and HgPh<sub>2</sub> (<sup>199</sup>Hg). <sup>b</sup> Hertz. <sup>c</sup> In THF.

ClHC=CHHgCl<sup>9</sup> and PhCOCH=CHHgCl<sup>10</sup> are longer (2.11 and 2.33 Å, respectively). Both PC1HgC1'P' units are planar with P=C bond distances of 1.644 (12) and 1.643 (11) Å, for molecules 1 and 2, respectively. This is rather short compared to other supermesityl-substituted phosphoalkenes, which fall into the range of 1.66–1.70 Å.<sup>2,4e,11</sup> These phosphoalkenes only differ in the substituent on carbon. Apparently, electron-donating substituents on carbon (Si,<sup>11</sup> Hg) shorten the bond, while electron-attracting ones increase it. This phenomenon is also observed for the C=C bond lengths of (E,E)-(HPhC=CH)<sub>2</sub>Hg and *trans*-stilbene (1.28 Å<sup>8</sup> and 1.30 Å,<sup>12</sup> respectively). The benzene rings are not completely planar, but they are, due to the *tert*-butyl groups, deformed toward a boat form. Similar, but even more pronounced distortion of Mes\* benzene rings has been reported.<sup>13</sup>

The crystal structure also helps to understand the stability of the *Z* configuration of 4 and 5 as compared to the surprising instability of the *E* compounds. It appears as if the mercury atom is attracted by and sandwiched in between the two benzene rings, whose mean planes are parallel. (Note that mercury resides on an inversion center!) The bond angles C1—P—C2 (5)° and 101.4 (5)°, respectively) and P—C1—Hg (127.4 (6)° and 124.1 (6)°, respectively) are small compared to analogous angles in Mes\*P=C(SiMe<sub>3</sub>)<sub>2</sub> (C1—P—C2 = 110°; P—C2—(Z)Si = 133°<sup>11a</sup>). This slightly bends the phenyl rings toward the mercury atom and reduces the distance between the mercury atoms and the centers of the phenyl rings to 3.571 (4) and 3.470 (4) Å. The mercury atom is placed asymmetrically above the Mes\* ring, with the closest distance to C2, C3, and C15 (3.252 (9), 3.549 (9), and 3.710 (10) Å, respectively, for molecule 1; 3.170 (10), 3.604 (10), and 3.442 (11) Å, respectively, for molecule 2). Interactions of mercury with  $\pi$  systems are known to occur at a distance ranging from 3 to 3.4 Å, which is close to the sum of the van der Waals radii of carbon and mercury.<sup>14</sup> We assume that this interaction of mercury with the  $\pi$  cloud of the phenyl rings stabilizes the *Z,Z* configuration. Another type of through-space interaction has been invoked by Prishchenko et al. to explain the stability of the phosphoalkene (Z)-(Me<sub>3</sub>Si)<sub>2</sub>NP=CHCl, namely, interaction of the electrophilic halogen atom and the lone electron pair at nitrogen, both being on the same side of the P=C bond.<sup>7f</sup>

### NMR Spectra

In Table IV relevant chemical shifts and coupling constants of (E)-4, (Z)-4, (E,E)-5, and (Z,Z)-5 are compared.

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From the crystal structure of (Z,Z)-5, all other stereoisomers of 4 and 5 could be identified by comparison of <sup>31</sup>P NMR chemical shifts (the *Z* isomers are more shielded), <sup>2</sup>J(PH) coupling constants (the <sup>2</sup>J(PH) for the *Z* isomers are larger), and <sup>2</sup>J(P<sup>199</sup>Hg) coupling constants (the <sup>2</sup>J(P<sup>199</sup>Hg) for the *Z* isomers are smaller). In all four compounds, both nuclei (H, Hg) with the largest coupling constant are located *cis* toward the phosphorus lone pair. This confirms the modified *cis* rule (*vide supra*) insofar as for the most electropositive nucleus, in *casu* mercury, the <sup>2</sup>J(P<sup>199</sup>Hg) coupling constant is much larger when it is *cis* to the phosphorus lone pair; moreover, the difference in  $\Delta^2J(\text{P}^{199}\text{Hg})$  between the *cis* and *trans* coupling is very large. For the less electropositive nucleus proton, however, the *cis* <sup>2</sup>J(PH) coupling (relative to the lone pair) is also larger than the *trans* coupling; this is opposite to the situation encountered with the group 14 nuclei silicon and tin, while for germanium, the *cis* and *trans* <sup>2</sup>J(PH) are equal.<sup>3</sup> Therefore, on the basis of the material available so far, we come to the conclusion that the *cis* rule always holds for the more electropositive substituent X in RP=CXY. For the second substituent Y, the relative size of <sup>2</sup>J(PY) seems to depend on the difference in electronegativity between the two substituents, ranging from *J*(*cis*):*J*(*trans*) < 1 for large differences in electronegativity to values of 1 or even >1 for small differences. In any case, the difference  $\Delta^2J(\text{cis, trans})$  is much less pronounced than that of the more positive nucleus.

The <sup>2</sup>J(P<sup>199</sup>Hg) coupling constants of (E)-4 and (Z)-4 are both larger than those of (E,E)-5 and (Z,Z)-5, respectively, probably indicating a higher *s*-character in the C—Hg bond. In accord with ref 3, but in contrast to results of Romanenko et al.,<sup>7i</sup> the <sup>1</sup>J(P=C) of the *Z* isomers are larger.

### Conclusions

The synthesis of phosphoalkene 1 from Mes\*PCl<sub>2</sub> and HCl<sub>3</sub> was further improved using 2 equiv of LDA.

The (phosphaalkenyl)mercury compounds (E)-4, (Z)-4, (E,E)-5, and (Z,Z)-5 were synthesized. The configuration of (Z,Z)-5 was determined by X-ray diffraction. From the NMR data (Table IV), the configurations of the other compounds [(E)-4, (Z)-4, (E,E)-5] could be assigned.

According to the crystal structure, a stabilizing interaction between the mercury atom and the phenyl ring exists. This may be the driving force for the isomerization of the *E* isomers (E)-4 and (E,E)-5 to the *Z* isomers (Z)-4 and (Z,Z)-5, and for the stability of the latter.

### Experimental Section

All experiments were performed in flame-dried glassware under a nitrogen atmosphere. NMR spectra were recorded on a Bruker AC 200 spectrometer (<sup>1</sup>H and <sup>13</sup>C), a Bruker WM 250 spectrometer (<sup>31</sup>P), or a Bruker MSL 400 spectrometer (<sup>199</sup>Hg). High-resolution mass spectra (HRMS) were recorded on a Finnigan MAT 5 spectrometer. Elemental analyses were performed by Microanalytisches Labor Pascher, Remagen, Germany.

(Diiodomethylene)(2,4,6-*tri-tert*-butylphenyl)phosphane (1). A solution of LDA in THF (83 mL, 0.6 M, 49.8 mmol) was added at -100 °C during 1 h to a solution of dichloro(2,4,6-*tri-tert*-butylphenyl)phosphine (8.6 g, 24.8 mmol) and iodoform (9.8

g, 24.8 mmol) in THF (200 mL). The reaction mixture was slowly warmed to room temperature. The solvent was evaporated at room temperature in vacuo, and the residue was extracted with pentane (400 mL). The pentane extract was evaporated at room temperature in vacuo, yielding orange crystals. Yield: 12.5 g, 23.5 mmol, 93%.  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  NMR and HRMS spectra were identical with those reported.<sup>3</sup>

**(*E,Z*)-[(Chloromercurio)methylene](2,4,6-tri-*tert*-butylphenyl)phosphane [(*E,Z*)-4].** A solution of *n*-BuLi in hexane (1.91 mL, 1.6 M, 3.06 mmol) was added during 15 min at  $-100^\circ\text{C}$  to a solution of (*E/Z*)-2<sup>3</sup> (1.25 g, 3.00 mmol) in THF (40 mL). The reaction mixture was stirred at  $-80^\circ\text{C}$  for 30 min and then cooled to  $-120^\circ\text{C}$ ; HgCl<sub>2</sub> (solid, 0.76 g, 2.80 mmol) was added in one batch. The reaction mixture was slowly warmed to room temperature. According to the  $^{31}\text{P}$  NMR spectrum of the reaction mixture, (*E*)-4 and (*Z*)-4 (ratio of 80:20) were the main products.  $^{31}\text{P}$  NMR (THF) for (*E*)-4:  $\delta$  311 (d,  $^2J(\text{PH}) = 27$  Hz,  $^2J(\text{P}^{199}\text{Hg}) = 1365$  Hz).  $^{31}\text{P}$  NMR (THF) for (*Z*)-4: vide infra. The solvent was evaporated at room temperature, and the residue was extracted with toluene. The toluene extract was evaporated in vacuo, and the residue was recrystallized from diethyl ether to yield colorless crystals (0.34 g, 0.66 mmol, 31%). From the  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  NMR spectra, it was apparent that the product isolated was not (*E*)-4 but (*Z*)-4.

**(*Z*)-[(Chloromercurio)methylene](2,4,6-tri-*tert*-butylphenyl)phosphane [(*Z*)-4].** A solution of *n*-BuLi in hexane (0.85 mL, 1.6 M, 1.36 mmol) was added during 10 min at  $-100^\circ\text{C}$  to a solution of (*Z*)-2<sup>3</sup> (0.54 g, 1.30 mmol) in THF (20 mL). The reaction mixture was stirred for 30 min at  $-80^\circ\text{C}$  and then cooled to  $-95^\circ\text{C}$ ; HgCl<sub>2</sub> (solid, 0.38 g, 1.40 mmol) was added in one batch. The reaction mixture was slowly warmed to room temperature. The solvent was evaporated in vacuo at room temperature, and the residue was extracted with diethyl ether. (*Z*)-4 was crystallized from diethyl ether. Yield: 0.34 g, 0.66 mmol, 51%.  $^1\text{H}$  NMR (CDCl<sub>3</sub>):  $\delta$  7.96 (d, 1 H,  $^2J(\text{HP}) = 29.6$  Hz,  $^2J(\text{H}^{199}\text{Hg}) = 83.9$  Hz, P=CH), 7.38 (s, 2 H, ArH), 1.44 (s, 18 H, *o*-*t*Bu), 1.29 (s, 9 H, *p*-*t*Bu).  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>):  $\delta$  183.0 (dd,  $^1J(\text{CP}) = 54.5$  Hz,  $^1J(\text{CH}) = 158$  Hz, P=C), 153.5 (s, *o*-Ar), 151.2 (s, *p*-Ar), 146.7 (d,  $^1J(\text{CP}) = 60.3$  Hz, *ipso*-Ar), 122.7 (dd,  $^1J(\text{CH}) = 154.5$  Hz,  $^3J(\text{CH}) = 6.3$  Hz, *m*-Ar), 38.1 (s, *o*-C(CH<sub>3</sub>)<sub>3</sub>), 34.7 (s, *p*-C(CH<sub>3</sub>)<sub>3</sub>), 34.4 (dq,  $^4J(\text{CP}) = 8.0$  Hz,  $^1J(\text{CH}) = 127$  Hz, *o*-C(CH<sub>3</sub>)<sub>3</sub>), 31.2 (q,  $^1J(\text{CH}) = 126$  Hz, *p*-C(CH<sub>3</sub>)<sub>3</sub>).  $^{31}\text{P}$  NMR (CDCl<sub>3</sub>):  $\delta$  333.6 (d,  $^2J(\text{PH}) = 30.5$ ,  $^2J(\text{P}^{199}\text{Hg}) = 368$  Hz).  $^{199}\text{Hg}$  NMR (CDCl<sub>3</sub>):  $\delta$  -1152 (br s, half-width 1000 Hz). HRMS for C<sub>19</sub>H<sub>30</sub><sup>36</sup>Cl<sup>204</sup>HgP: calcd 528.1454, found 528.146.

**(*E,E*)-Mercuriobis[methylene(2,4,6-tri-*tert*-butylphenyl)phosphane] [(*E,E*)-5].** A solution of *n*-BuLi in hexane (2.1 mL, 1.6 M, 3.36 mmol) was added during 10 min at  $-100^\circ\text{C}$  to a solution of (*E/Z*)-2 (1.34 g, 3.22 mmol) in THF (50 mL). The reaction mixture was stirred at  $-80^\circ\text{C}$  for 30 min and then cooled to  $-130^\circ\text{C}$ ; HgCl<sub>2</sub> (solid, 0.44 g, 1.61 mmol) was added in one batch. The reaction mixture was slowly warmed to room temperature. The solvent was evaporated in vacuo at room temperature, and the residue was extracted with pentane. The pentane extract was concentrated and cooled to yield a colorless powder of (*E,E*)-5. Yield: 0.59 g, 0.75 mmol, 47%. Mp: 140–142  $^\circ\text{C}$  dec.  $^1\text{H}$  NMR (CDCl<sub>3</sub>):  $\delta$  8.45 (d, 2 H,  $^2J(\text{PH}) = 24.2$  Hz,  $^2J(\text{H}^{199}\text{Hg}) = 93.1$  Hz, P=CH), 7.31 (s, 4 H, ArH), 1.48 (s, 36 H, *o*-*t*Bu), 1.27 (s, 18 H, *p*-*t*Bu).  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>):  $\delta$  203.3 (dd,  $^1J(\text{CP}) = 75.1$  Hz,  $^3J(\text{CP}) = 7.2$  Hz,  $^1J(\text{CH}) = 151$  Hz, P=C), 152.4 (s, *o*-Ar), 149.5 (s, *p*-Ar), 144.2 (d,  $^1J(\text{CP}) = 75.5$  Hz, *ipso*-Ar), 122.0 (dd,  $^1J(\text{CH}) = 152.5$  Hz,  $^3J(\text{CH}) = 6.1$  Hz, *m*-Ar), 38.1 (s, *o*-C(CH<sub>3</sub>)<sub>3</sub>), 34.8 (s, *p*-C(CH<sub>3</sub>)<sub>3</sub>), 33.9 (dq,  $^4J(\text{CP}) = 7.6$  Hz,  $^1J(\text{CH}) = 125$  Hz, *o*-C(CH<sub>3</sub>)<sub>3</sub>), 31.3 (q,  $^1J(\text{CH}) = 125$  Hz, *p*-C(CH<sub>3</sub>)<sub>3</sub>).  $^{31}\text{P}$  NMR (CDCl<sub>3</sub>):  $\delta$  315.8 (d,  $^2J(\text{PH}) = 24.4$  Hz,  $^2J(\text{P}^{199}\text{Hg}) = 804.6$  Hz).  $^{199}\text{Hg}$  NMR (CDCl<sub>3</sub>):  $\delta$  -600.0 (t,  $^2J(\text{HgP}) = 813$  Hz). HRMS for C<sub>38</sub>H<sub>60</sub><sup>200</sup>HgP<sub>2</sub>: calcd 778.3854, found 778.385.

**(*Z,Z*)-Mercuriobis[methylene(2,4,6-tri-*tert*-butylphenyl)phosphane] [(*Z,Z*)-5].** A solution of *n*-BuLi in hexane (2.0 mL, 1.6 M, 3.20 mmol) was added during 10 min at  $-100^\circ\text{C}$  to a solution of (*Z*)-2 (1.34 g, 3.22 mmol) in THF (50 mL). The reaction mixture was stirred at  $-80^\circ\text{C}$  for 30 min and then cooled to  $-95^\circ\text{C}$ ; HgCl<sub>2</sub> (solid, 0.42 g, 1.55 mmol) was added in one batch.

The reaction mixture was slowly warmed to room temperature. The solvent was evaporated in vacuo at room temperature, and the residue was extracted with pentane. The pentane extract was evaporated to dryness, and the residue was crystallized at  $-80^\circ\text{C}$  from pentane to yield colorless crystals of (*Z,Z*)-5. Yield: 0.75, 0.97 mmol, 63%. Mp: 200.5–201.5  $^\circ\text{C}$ .  $^1\text{H}$  NMR (CDCl<sub>3</sub>):  $\delta$  8.15 (d, 2 H,  $^2J(\text{HP}) = 28.3$  Hz,  $^2J(\text{H}^{199}\text{Hg}) = 38.1$  Hz, P=CH), 7.31 (s, 4 H, ArH), 1.44 (s, 36 H, *o*-*t*Bu), 1.35 (s, 18 H, *p*-*t*Bu).  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>):  $\delta$  208.6 (dd,  $^1J(\text{CP}) = 54.1$  Hz,  $^3J(\text{CP}) = 4.2$  Hz,  $^1J(\text{CH}) = 145$  Hz, P=C), 153.6 (s, *o*-Ar), 149.3 (s, *p*-Ar), 148.0 (d,  $^1J(\text{CP}) = 62.2$  Hz, *ipso*-Ar), 121.2 (dd,  $^1J(\text{CH}) = 153.2$  Hz,  $^3J(\text{CH}) = 6.5$  Hz, *m*-Ar), 38.0 (s, *o*-C(CH<sub>3</sub>)<sub>3</sub>), 34.7 (s, *p*-C(CH<sub>3</sub>)<sub>3</sub>), 34.3 (dq,  $^4J(\text{CP}) = 8.0$  Hz,  $^1J(\text{CH}) = 125$  Hz, *o*-C(CH<sub>3</sub>)<sub>3</sub>), 31.3 (q,  $^1J(\text{CH}) = 125$  Hz, *p*-C(CH<sub>3</sub>)<sub>3</sub>).  $^{31}\text{P}$  NMR (CDCl<sub>3</sub>):  $\delta$  343.4 (d,  $^2J(\text{PH}) = 28.0$  Hz,  $^2J(\text{P}^{199}\text{Hg}) = 182.2$  Hz).  $^{199}\text{Hg}$  NMR (CDCl<sub>3</sub>):  $\delta$  -818.1 (tt,  $^2J(\text{HgP}) = 182$  Hz,  $^2J(\text{HgH}) = 38$  Hz). HRMS for C<sub>38</sub>H<sub>60</sub><sup>200</sup>HgP<sub>2</sub>: calcd 778.3854, found 778.385. Anal. Calcd for C<sub>38</sub>H<sub>60</sub>P<sub>2</sub>Hg: C, 58.56; H, 7.76; P, 7.95; Hg, 25.74. Found: C, 58.35; H, 7.81; P, 7.91; Hg, 25.50.

**Crystal Structure Determination and Refinement of (*Z,Z*)-5.** Crystal data and numerical details of the structure determination are given in Table IV. A colorless, block-shaped crystal, suitable for X-ray structure determination, was sealed in a Lindemann-glass capillary and transferred to an Enraf-Nonius CAD-4F diffractometer for data collection. Lattice parameters were determined by least-squares fitting of the SET4 setting angles of 25 reflections with  $10.7^\circ < \theta < 15.8^\circ$ . The unit-cell parameters were checked for the presence of higher lattice symmetry.<sup>15</sup> All data were collected with  $\omega/2\theta$  scan mode. Data were corrected for *Lp* and for the observed linear decay (<6%) of the reference reflections during 120 h of X-ray exposure time. Absorption correction was applied using the DIFABS procedure.<sup>16</sup> Standard deviations of the intensities as obtained by counting statistics were increased according to an analysis of the excess variance of the reference reflections:  $\sigma^2(I) = \sigma_{\text{count}}^2(I) + (0.0054I)^2$ .<sup>17</sup> The structure was solved by automated Patterson methods.<sup>18</sup> Refinement of *F* was carried out by full-matrix least-squares techniques.<sup>19</sup> The hydrogen atoms were included in the refinement on calculated positions (C–H = 0.98 Å) riding on their carrier atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters; the hydrogen atoms were refined with two common isotropic thermal parameters, one for the methyl groups and one for other hydrogen atoms of 0.101 (6) and 0.02 (1) Å<sup>2</sup>, respectively. Weights were introduced in the final refinement cycles. Convergence was reached at *R* = 0.0497 and *R*<sub>w</sub> = 0.0313. Neutral atomic scattering factors were taken from Cromer and Mann,<sup>20</sup> anomalous-dispersion corrections from Cromer and Liberman.<sup>21</sup> Geometrical calculations and illustrations were performed with PLATON.<sup>22</sup> Calculations were carried out on a DECstation 5000.

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**Supplementary Material Available:** Tables of anisotropic thermal parameters, all H atom parameters, bond lengths, bond angles, and crystal data and thermal motion ellipsoid plots (9 pages). Ordering information is given on any current masthead page.

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