α-Mercurio-Substituted Phosphorus Ylides: A Simple Route to Vinylmercury Compounds☆

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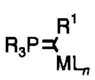
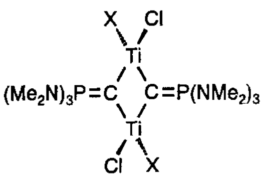
The synthesis of novel α-mercurio-substituted phosphorus ylides, $Ph_3P=CR[HgN(SiMe_3)_2]$ **3a–d** (R = Me, Et, *i*Pr, Ph) is easily accomplished by mixing equivalent amounts of a phosphorus ylide **1a–d** with $Hg[N(SiMe_3)_2]_2$ in an inert solvent. These organometallic compound are completely characterized including an X-ray analysis of **3a**. Their reaction with benzaldehyde yields vinylmercury amides (*E*)/(Z)-$PhHC=CR[HgN(SiMe_3)_2]$ **4a–d**. In reactions involving **3a–c** the stereochemistry [favored formation of (*E*)-**4a** (≈72–83%) and (Z)-**4b**, **c** (≈60–73%)] in the absence of a lithium salt is contrary to the stereochemistry of the established Wittig olefination reaction with non-stabilized phosphorus ylides like **1a–d**. From the reported results, the preliminary conclusion is drawn that the stereochemistry is mainly controlled by steric interactions. Only in one case a remarkable salt effect is observed. When **3c** reacts with benzaldehyde in the presence of LiBr and THF as solvent up to 95% of (*E*)-**4c** is formed. The semistabilized ylide **3d** gives under all conditions studied a 50:50 mixture of (*E*)/(Z)-**4d**. The vinylmercury amides **4a**, **c** are cleaved by hydrous NaOH to yield divinylmercury compounds (*E*,*E*)-$(PhHC=CR)_2Hg$ and (Z,Z)-$(PhHC=CR)_2Hg$ (R = Me: **7a**; R = *i*Pr: **7c**). The compound **4d** is cleanly cleaved by $NaBH_4$ in hydrous 3 M NaOH to yield a 50:50 mixture of *cis*- and *trans*-stilbene (**8**).

The synthesis of phosphorus ylides **I** with metal substituents at the ylidic carbon atom has been explored intensively[1]. Their reactivity and applications in organometallic chemistry, however, have only recently been investigated. Based on the reaction of cyclic α-titaniophosphorus ylides **II** with aromatic aldehydes Hughes et al. have developed a synthesis of allenes[2]. A stable chromaoxetane **III** has been synthesized by Sundermeyer et al. from an imidochromyl(VI)-substituted phosphorus ylide and diphenylketene[3].

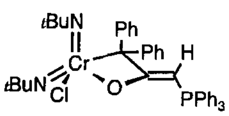


I

R: alkyl, aryl, amino
R¹: various substituents



II X = NMe₂, Cl



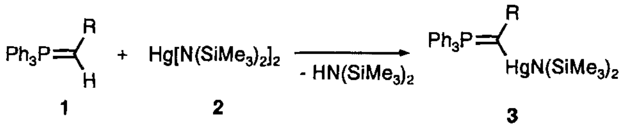
III

In these ylides depletion of the negative charge at the ylidic carbon atom into non-occupied d orbitals at the metal center in a formally high oxidation state occurs by (d-p)π interaction. Consequently, in reactions with carbonyl compounds the metal-carbon (d-p)π bond will be involved as is expected for Schrock-type carbenes[4]. Theoretical work predicts that σ donors as well as π acceptors will stabilize phosphorus ylides[5]. If there are no vacant d orbital functions available on the metal center, its σ donor capability will enhance the basicity and eventually the reactivity of the ylide. For that reason, α-metalated ylides with alkali or alkaline earth metal centers[6] or metal centers of group 11 and 12 have a high synthetic potential.

Results and Discussion

In this work we describe a very simple synthesis of α-mercurio-substituted phosphorus ylides and their transformation to vinylmercury compounds. Subsequently, these may be either reduced to the corresponding olefins or disproportionated to divinylmercury compounds. The first mercurated ylides have been described by Nesmeyanov and Schmidbaur[7]. We have now found a new synthesis of α-mercurio-substituted phosphorus ylides involving the reaction of alkylidene- or arylidenephosphoranes **1** with mercury bis[bis(trimethylsilyl)amide] (**2**) which may be easily performed on a multigram scale (Scheme 1).

Scheme 1



	a	b	c	d
R	Me	Et	*i*Pr	Ph

0009–2940/94/0707–1177 $ 10.00+.25/0

If a toluene solution of **1a**–**d** is mixed with one equivalent of **2** at room temperature $^{31}P\{^{1}H\}$- and ^{1}H-NMR spectra indicate the quantitative formation of compounds **3a**–**d** and hexamethyldisilazane. Recrystallization from toluene/*n*-hexane (1:5) gives in every case analytically pure microcrystalline products which are highly sensitive to hydrolysis. The isolated yield of the ylides **3a**–**d** is somewhat lower because of their high solubility in organic solvents. The compounds can be stored under argon for several weeks without decomposition. The signals in the $^{31}P\{^{1}H\}$-NMR spectra of **3a**–**d** are slightly shifted to lower field compared to the ylides **1a**–**d**. However, they lie still in the range expected for alkylidene- or arylidenetriphenylphosphoranes[8]. The resonances are accompanied by satellites due to coupling with the ^{199}Hg nucleus. In the $^{199}Hg\{^{1}H\}$-NMR spectra of **3a**–**d** doublets with coupling constants $^{2}J(^{199}Hg^{31}P)$ ranging from 520 to 560 Hz are observed which are characteristic of these mercurio-substituted ylides. The chemical shifts $\delta(^{199}Hg)$ lie within the expected range[9] and show an interesting sensitivity to the kind of substituent R attached to the ylidic carbon atom. Replacement of the methyl group in **3a** by an ethyl group in **3b** or isopropyl group in **3c** causes a regular downfield shift of the ^{199}Hg resonance of approximately 22 ppm per additional methyl group. The phenyl-substituted derivative **3d** on the other hand shows its resonance almost 100 ppm upfield from **3a**–**c** at $\delta = -614$. The signals of the ylidic carbon atoms in the $^{13}C\{^{1}H\}$-NMR spectra are considerably downfield shifted by more than 30 ppm compared to **1a**–**d**. This is attributed to a pronounced heavy atom effect of the σ-bound mercury center[10]. We have further characterized one of the mercurio-substituted phosphoranes **3a**–**d** by an X-ray structure analysis. Suitable crystals of **3a** have been grown from cold toluene/*n*-hexane solutions. The result is shown as a SCHAKAL plot[11] in Figure 1.

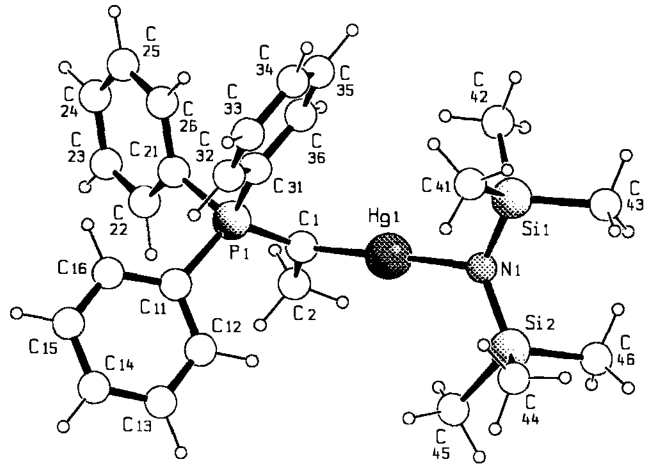
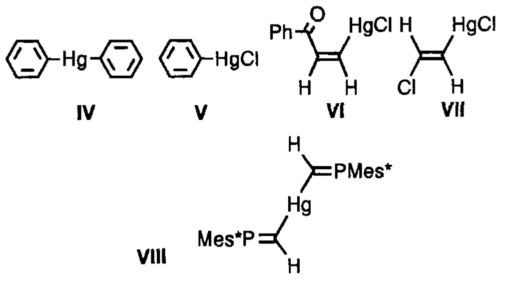


Figure 1. Molecular structure of **3a**; selected bond lengths [Å] and angles [°]: Hg1–C1 2.027(2), Hg1–N1 2.068(6), P1–C1 1.686(7), C1–C2 1.512(10), Si1–N1 1.705(6), Si2–N1 1.711(6); C2–C1–P1 120.0(6), C2–C1–Hg1 118.9(5), P1–C1–Hg1 117.8(4), C1–Hg1–N1 175.4(3), Si1–N1–Hg1 115.6(3), Si2–N1–Hg1 115.2(3), Si1–N1–Si2 128.0(4)

The coordination sphere of the mercury center deviates slightly from linearity [C–Hg–N 175.4(3)°]. The Hg–C bond length [2.027(7) Å] is rather short in comparison with other mercury compounds in which the mercury center is attached to a sp^2-configurated carbon atom. The Hg–C distances in $(C_6H_5)_2Hg$ (**IV**) or C_6H_5HgCl (**V**) as prototypes are 2.085 and 2.05 Å long[12]. However, much longer bonds are observed in the vinylmercury compounds *cis*-(PhCO)HC=CHHgCl (**VI**) (2.33 Å)[13] and *trans*-ClHC=CHHgCl (**VII**) (2.11 Å)[14].



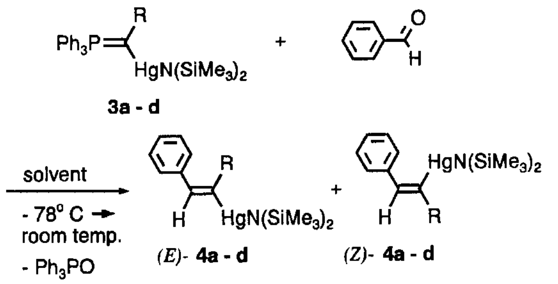
Short Hg–C distances, on the contrary, have recently been reported by Bickelhaupt et al. to exist in a bis(phosphaalkenyl)mercury compound, (*Z*,*Z*)-(Mes*P=CH)$_2$Hg (**VIII**) (2.042, 2.079 Å; Mes* = 2,4,6-tBu$_3$C$_6$H$_2$)[15]. Obviously, the broad range of Hg–C(sp^2) distances $\Delta r \approx 0.3$ Å is caused by electrostatic interactions between the electropositive mercury center and the neighboring carbon center. This is supported by an PM3[16] estimation of atomic charges $q_{(PM3)}$ of the hydrocarbons $H_2C=X$ [X = CH(COPh), CHCl, PPh, PPh$_3$] were the negative charge on the carbon center of the CH$_2$ unit increases [$q_{(PM3)}$: −0.054, −0.162, −0.492, −1.024 e, respectively] as the Hg–C distances in R–Hg–CH=X decreases. Such rather dramatic effects on bond lengths data caused by electronic changes in the ligands are not unexpected and are characteristic of flat potential curves of weak bonds. Correlations like this may be useful for the understanding and prediction of the stability of organomercury compounds. The Hg1–N1 bond [2.068(6) Å] is longer than the Hg1–C1 distance and within the range expected for Hg–N bond lengths (≈2.07 Å[12]). The nitrogen center of the (Me$_3$Si)$_2$N group is coordinated in an almost planar manner [$\Sigma^0 = 358.8°$].

Another interesting feature of the molecular structure of **3a** concerns the pyramidalization of the ylidic carbon atom. The sum of bond angles Σ^0 amounts to 356.7°, and the p orbital function perpendicular to the C2–C1–Hg1 plane which is used to describe the π electron density at the ylidic carbon atom is almost in plane (deviation 12.6°) with the P1–C11 bond. A number of phosphorus ylides with comparably pyramidalized ylidic carbon atoms are known meanwhile[17] indicating the broad soundness of the well-established concept of negative hyperconjugation in order to describe the electronic properties of ylides[5]. The P1–C1 distance of 1.686(7) Å lies within the range of alkyl-substituted (unstabilized) ylides[17].

Reactivity

The mercurated ylides **3a**–**d** react with equimolar amounts of benzaldehyde in toluene or THF solution (Scheme 2).

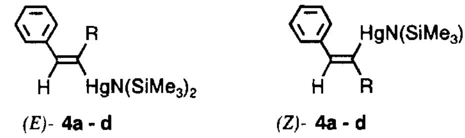
Scheme 2



	a	b	c	d
R	Me	Et	*i*Pr	Ph

In the case of **3a** the red color of the solution fades immediately when the aldehyde is added at −78°C while the reaction between **3b**, **c**, and **d** with the aldehyde takes place at temperatures of −40, 0, and 25°C, respectively. The triphenylphosphane oxide (TPPO) formed in the reaction can be removed by precipitation from concentrated *n*-hexane solutions of the reaction mixtures at −78°C. In every case, the amount of isolated TPPO corresponds with 95% conversion of the reaction. The desired products, the vinylmercury amides **4a**–**d**, are isolated as oils after evaporation of all volatile components from the *n*-hexane filtrates. These raw materials are characterized by ^1H- and $^{199}Hg\{^1H\}$-NMR spectra. Attempted purification of **4a**–**d** by distillation has led to decomposition. The same results are obtained when **3a**–**d** are synthesized and allowed to react without isolation from the reaction mixture with aldehyde to give **4a**–**d** in a one-pot procedure. In every case, we have observed signals which we have assigned to mixtures of *Z* and *E* isomers. While the vinylmercury amides **4a**, **b**, and **d** are obtained with reasonable purity the isopropyl-substituted derivative **4c** (R = *i*Pr) is not. Up to 50% of the isolated material have undergone a ligand exchange reaction, and the divinylmercury compound **7c** (isomer mixture) and mercury amide **2** (^{199}Hg: $\delta = -1032.9$) are detected by $^{199}Hg\{^1H\}$-NMR spectroscopy. In the case of **4b** this ligand exchange reaction proceeds in some experiments to give approx. 10% of **7b** and **2**. Surprisingly, when the reactions are performed in toluene/THF mixtures (5:1 vol-%) or in THF as solvents, and LiBr is added to these solutions rearrangements are effectively suppressed. The (co)solvent THF alone without LiBr addition has no effect. Ligand exchange of unsymmetrical mercury compounds RHgX to R_2Hg and HgX_2 in the presence of a base has already been observed by Beletskaya et al.[18]. One obvious explanation of the LiBr effect in the reactions described here is therefore a diminuation of the basicity of the ylides **3a**–**d** by complexation.

Table 1. Solvent dependence of the reaction of $Ph_3P{=}CR[HgN(SiMe_3)_2]$ (**3a**–**d**) with benzaldehyde with formation of **4a**–**d**



	Toluene	Toluene LiBr	Toluene/THF	Toluene/THF LiBr	THF	THF LiBr	Isomer Distribution
4a[a]	72:28	76:24	83:17	81:19	74:26	78:22	*(E)/(Z)*
4b[a,b]	37:63	39:61	35:65	46:54	29:71	38:62	*(E)/(Z)*
4c[a]	33:67	32:68	41:59	95:5	27:73	88:12	*(E)/(Z)*
4d[a]	58:42	55:45	53:47	50:50	47:53	52:48	*(E)/(Z)*
5[a]	90:10	87:13	92:8	60:40	91:9	68:32	*(Z)/(E)*

[a] Reaction started at −78°C and mixture warmed to room temp. – [b] The isomer distribution changes slightly when the reaction is performed at room temp. in THF: (*E*)/(*Z*) without LiBr 36:64; (*E*)/(*Z*) in the presence of LiBr 53:47.

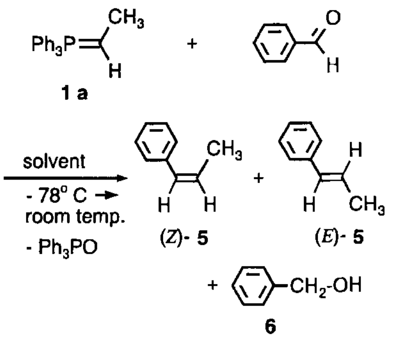
Stereochemistry

The stereochemistry of the reactions of phosphorus ylides with carbonyl compounds (Wittig reaction) has been extensively studied[19]. The reactions of alkyl-substituted ylides (unstabilized) give olefins with predominantly *Z* configuration while aryl-substituted ylides (semistabilized) are converted into 1:1 mixtures of *Z* and *E* isomers. Addition of lithium salts leads preferentially to the formation of the *E* isomer when alkyl-substituted ylides are employed in the Wittig reaction, whereas an excess of the *Z* isomer is formed in the olefination reaction of semistabilized ylides with aldehydes. We have investigated the stereochemistry of the olefination reaction of the mercurated ylides **3a**–**d** under a varity of reaction conditions (Table 1). The stereochemistry of the products **4a**–**c** was assigned on the basis of the allylic $^4J_{HH}$ coupling constants which are larger in the case the allylic hydrogen center has a *cis* orientation with respect to the vinylic hydrogen center[20] (corresponding to the *E* isomer of **4a**–**c**). Furthermore, the signals of the allylic hydrogen centers of **4a**–**c** are shifted to lower magnetic field strength when they are affected by the ring current effect of the *cis*-orientated phenyl group (corresponding to the *Z* isomer of **4a**–**c**). Provided that these assumptions are correct, the *E* isomer of **4a**–**d** shows the more high-field shifted ^{199}Hg-NMR resonance while the *Z* exhibits its ^{199}Hg-NMR resonance approximately 60–100 ppm downfield-shifted, which might be again due to the magnetic anisotropy of the phenyl group *cis*-oriented with respect to the mercury nucleus (for further details see the experimental part).

Since most of the reactions have been carried out at low temperature (−78°C) we have additionally studied the reaction of the non-metalated ylide **1a** with benzaldehyde as a "reference reaction" under similar conditions (Scheme 3).

The trend in the *E*/*Z* isomer distribution of the resulting olefin **5** described in the literature[19c] is almost reproduced. Without addition of LiBr the isomer (*Z*)-**5** predominates

Scheme 3

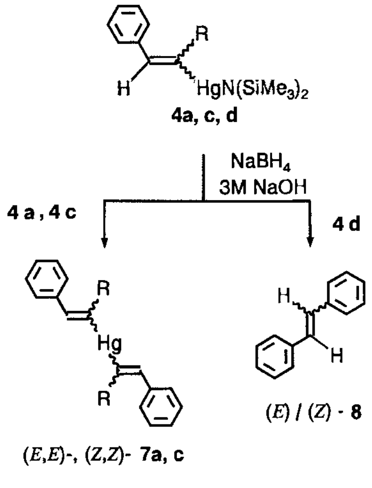


(≈90%) when the olefination is performed in toluene, toluene/THF mixtures, or THF alone as reaction medium. Addition of LiBr yields the isomer (*E*)-**5** up to ≈40%. In all experiments, however, considerable amounts of benzyl alcohol (**6**) have been detected by gas chromatography. Interestingly, Olah et al. have reported on the reduction of adamantanone and benzophenone to the corresponding alcohols upon reaction with ylides $Ph_3P{-}CR_2$ (R = H, Me, Ph) as well[21]. This unexpected reaction path is explained by the occurrence of a single-electron transfer (SET) from the ylide to the carbonyl compound. Recently, a similar observation has been made by Nagase and coworkers. On the basis of measurements of carbonyl-^{14}C kinetic isotope effects in the Wittig reaction of nonstabilized ylides with benzaldehyde they propose an electron transfer as the initial step leading to the oxaphosphetane[22]. Although further quantification is necessary, our findings are in line with the assumption that electron-transfer reactions and radicals may be involved in the Wittig reaction which is still a miracle concerning its stereochemistry[23]. Note that phosphorus ylides have very low first vertical ionization potentials[24].

In the reaction of the mercurated ylides **3a** and **3d** with benzaldehyde the stereochemistry of the products **4a** and **4d** is not influenced by the addition of LiBr or a change of the solvent within experimental error (±10% determined by integration of the well separated ^{199}Hg-NMR signals). Approximately 77% of (*E*)-**4a** and 23% of (*Z*)-**4a** are formed and (*E*)-**4d**/(*Z*)-**4d** are obtained as a 50:50 isomer mixture. Note that the *E* isomers of the vinylmercury compounds correspond with the *Z* isomer of **5**. This means that the replacement of a hydrogen atom in **1a** by a $HgN(SiMe_3)_2$ moiety to give **3a** slightly favors the isomer in which the methyl group and phenyl group occupy the 1,2-*trans* position of the olefin. However, the isomers with *cis* orientation of methyl and phenyl group [(*Z*)-**5**, (*E*)-**4a**] predominate in both cases over the other isomers. The isomer distribution changes when both the ethyl group and the mercury amide moiety are bound to the ylidic carbon atom. Now, a *trans* arrangement of the phenyl and the ethyl group as in (*Z*)-**4b** clearly predominates (≈65%). There might be a weak effect of added LiBr in favor of isomer (*E*)-**4b**, and a mixture of about 50% of both isomers is obtained. (This effect is somewhat more pronounced when the reaction is performed at room temperature. We find a *E*/*Z* ratio of 36:64 without and of 53:47 in the presence of LiBr if THF is used as solvent.) The reaction of the isopropyl-substituted mercurated ylide **3c** with benzaldehyde is most interesting. If the reaction is performed without a lithium salt an isomer mixture comparable to the one obtained with the ethyl derivative **3b** is observed [≈33% (*E*)-**4c**, ≈67% (*Z*)-**4c**). The addition of LiBr has a pronounced effect on the isomer distribution. Now (*E*)-**4c** is formed in about 91% yield in toluene or THF solution. This isomer with the bulky isopropyl group and the phenyl group in 1,2-*cis* position is certainly more sterically encumbered than the isomer (*Z*)-**4c**. While in "usual" Wittig reactions with alkyl-substituted phosphorus ylides the sterically less favored *Z* olefin is formed in the absence of a lithium salt and the sterically more favored *E* olefin in the presence of a lithium salt, the reverse applies to the mercurated ylides **3a–d**. We have no straightforward explanation for this observation at the moment. Because all reactions have been performed at low temperatures the addition of LiBr to pure toluene solutions has no significant effect on the isomer distribution in reactions with **1a** or **3c** due to the insolubility of the salt. Separation of the byproduct TPPO, however, is facilitated when LiBr is present in all experiments. In none of the reactions of the ylides **3a–d** we have found evidence for the reduction of benzaldehyde to benzyl alcohol.

Finally, we have studied the hydrolytic reduction of the vinylmercury amides with alkaline solutions of $NaBH_4$. In the case of **4a** and **4c** no cleavage of the Hg–C bond is observed[25], and the divinylmercury compounds **7a** and **7c** are obtained (Scheme 4).

Scheme 4



	a	c	d
R	Me	*i*Pr	Ph

Consequently, addition of 3 M NaOH to the solutions containing **4a, c** – after **3a** and **3c** have been treated with benzaldehyde – leads to **7a** and **7c** as well. Remarkably, only two isomers of three possible ones which differ in the stereochemistry of the carbon carbon bond [*E*/*E*, *E*/*Z*, and *Z*/*Z*] are detected by ^{199}Hg- and ^{1}H-NMR spectroscopy in a ratio which corresponds with the isomer ratio of the initially formed vinylmercury amides. Hence, we assign the isomers of **7a** and **7c** to *E*/*E* and *Z*/*Z* combinations underlined by the magnitude of the $^{4}J_{HH}$ coupling constant. For unknown reasons the *E*/*Z* combination is not observed. In contrast, the vinylmercury amide **4d** is cleanly hydrolyzed by alkaline $NaBH_4$ solutions to give Hg, HgO, and mixtures of *cis*- and *trans*-stilbene [(*Z*)-**8** and (*E*)-**8**], respectively. With the arguments outlined above, the facile Hg−C bond rupture occurring in the course of this reaction can be rationalized by regarding the charge distribution in the hydrocarbons $PhHC{=}\mathit{C}HPh$ and $PhHC{=}\mathit{C}HMe$ [*C* in *cis-*/*trans*-stilbene: $q_{(PM3)} = -0.088$ e, -0.097 e; *C* in *cis-*/*trans*-$PhHC{=}\mathit{C}HMe$: $q_{(PM3)} = -0.125$ e, -0.138 e). The latter would be the product of Hg−C bond cleavage in **4a**. However, the carbon center of the CHMe fragment to which the $HgN(SiMe_3)_2$ moiety is bound bears a higher negative charge, and a stronger Hg−C bond is expected in the vinylmercury compound **4a** compared to **4d**. The isomer ratio found in **8** (50:50) again resembles the one estimated for **4d**.

Conclusions

Mercurated phosphorus ylides are easily synthesized by treating equimolar amounts of an alkyl- or aryl-substituted phosphorus ylide with mercury bis[bis(trimethylsilyl)amide] (**2**). Preliminary results show that this type of reaction which proceeds with the extrusion of the inert amine $HN(SiMe_3)_2$ in homogeneous solution may be extended to metal amides like $Cd[N(SiMe_3)_2]_2$, $Zn[N(SiMe_3)_2]_2$, $Sn[N(SiMe_3)_2]_2$, and other transition metal amides like $Fe[N(SiMe_3)_2]_3$ and $Mn[N(SiMe_3)_2]_2$. Therefore, it may be a promising general route to novel organometallics. The parent phosphorus ylide $Ph_3P{=}CH_2$ reacts with **2** to give a complex product which could not be characterized satisfactorily to date due to its extreme sensitivity. In the case of the isolated mercurated phophorus ylides, subsequent reaction with benzaldehyde proceeds like a normal Wittig olefination to give vinylmercury amides and triphenylphosphane oxide. The stereochemistry, however, is different from the one of simple alkyl-substituted phosphorus ylides, i.e. steric interactions seem to dominate the course of the reaction in the absence of lithium salts. Given that steric interactions control the stereochemistry of the olefination, the data listed in Table 1 indicate that a methyl group is sterically less demanding than a $HgN(SiMe_3)_2$ moiety which, on the other hand, is less sterically demanding than an ethyl or isopropyl group. In one case we could observe a significant lithium salt effect, and remarkably the sterically less favored product is formed in the presence of LiBr. Again, this is in contrast to the "ordinary" Wittig olefination in which the sterically less encumbered (*E*)-olefin is formed under comparable conditions. We are currently investigating the reaction of mercurated ylides with other carbonyl compounds and further transformations of the vinylmercury compounds synthesized in this way.

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Experimental

Mercury bis[bis(trimethylsilyl)amide] (**2**)[26] and the phosphoranes **1a**−**d**[27] were prepared by literature methods. All solvents were carefully dried and freshly distilled under nitrogen. All operations were carried out in flame-dried glassware under dry argon by using a modified Schlenk technique. − NMR: FX-90Q (^{1}H: 89.55 MHz, ^{13}C: 22.49 MHz, ^{29}Si: 17.75 MHz, ^{31}P: 36.19 MHz, ^{199}Hg: 15.95 MHz), Bruker AC 200 (^{1}H: 200.132 MHz, ^{13}C: 50.323 MHz) with Me_4Si (int.), 85% H_3PO_4 (ext.) and Me_2Hg (ext.) as standards. − Melting points: sealed capillaries, uncorrected.

General Procedure for the Preparation of the Mercurio-Substituted Phosphoranes **3a**−**d**: Phosphoranes **3a**−**d** were formed when a red to orange solution of the phosphorane **1** (**a**, **b**, **c**, or **d**) was treated with equimolar amounts of mercury bis[bis(trimethylsilyl)amide] (**2**) at room temp. The color became yellow and the $^{31}P\{^{1}H\}$-NMR spectra of the crude reaction mixture indicated complete reaction within seconds. After 10 min the reaction mixtures were concentrated in vacuo to 1/5 of their volume, and 20 ml *n*-hexane was added. After cooling at −78°C for 14 h the products were collected and washed once with small quantity of *n*-hexane.

$Ph_3P{=}C(Me)HgN(SiMe_3)_2$ (**3a**): In a typical experiment 1.5 g of phosphorane **1a** (5.17 mmol) was treated with 2.69 g of **2** in 20 ml of toluene. Yield: 2.28 g (68%) of orange crystals, which decomposed immediately on exposure to air; m.p. 81−85°C. − ^{1}H NMR (C_6D_6): δ = 0.21 (s, 18H, $SiMe_3$), 2.40 (d, 3H, $^{3}J_{HP}$ = 21.2 Hz, CH_3), 6.90−7.19 [m, 9H, *m*/*p*-H (Ph)], 7.55−7.86 [m, 6H, *o*-H (Ph)]. − $^{13}C\{^{1}H\}$ NMR (C_6D_6): δ = 5.58 (s, $SiMe_3$), 15.83 (d, $^{2}J_{CP}$ = 2.6 Hz, CH_3), 40.75 (d, $^{1}J_{CP}$ = 84.9 Hz, PC_{ylide}), 128.61 [d, $^{3}J_{CP}$ = 11.1 Hz, *m*-C (Ph)], 131.02 [d, $^{4}J_{CP}$ = 2.8 Hz, *p*-C (Ph)], 133.32 [d, $^{2}J_{CP}$ = 9.0 Hz, *o*-C (Ph)], 134.08 [d, $^{1}J_{CP}$ = 82.5 Hz, *ipso*-C (Ph)]. − $^{29}Si\{^{1}H\}$ NMR: δ = −1.52. − $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ = 19.81 ($^{2}J_{HgP}$ = 564.5 Hz). − $^{199}Hg\{^{1}H\}$ NMR (C_6D_6, 0.25 M, 298 K): δ = −529 ($^{2}J_{HgP}$ = 564.5 Hz). − No satisfactory C, H analysis could be obtained due to the high sensitivity of **3a** to hydrolysis.

$Ph_3P{=}C(Et)HgN(SiMe_3)_2$ (**3b**): In a typical experiment 1.5 g of phosphorane **1b** (4.9 mmol) was treated with 2.57 g of **2** in 20 ml of toluene. Yield: 2.43 g (74%) of orange crystals, m.p. 82−86°C. − ^{1}H NMR (C_6D_6): δ = 0.22 (s, 18H, $SiMe_3$), 1.33 (td, 3H, $^{3}J_{HH}$ = 7.1, $^{4}J_{HP}$ = 1.7 Hz, Me), 2.67 (qd, 2H, $^{3}J_{HH}$ = 7.1, $^{3}J_{HP}$ = 15.9 Hz, CH_2), 6.95−7.20 [m, 9H, *m*/*p*-H (Ph)], 7.60−7.73 [m, 6H, *o*-H (Ph)]. − $^{13}C\{^{1}H\}$ NMR (C_6D_6): δ = 5.66 (s, $SiMe_3$), 24.17 (d, $^{2}J_{CP}$ = 4.7 Hz, CH_2), 24.72 (d, $^{3}J_{CP}$ = 16.8 Hz, Me), 52.09 (d, $^{1}J_{CP}$ = 82.4 Hz, PC_{ylide}), 127.52 [d, $^{3}J_{CP}$ = 10.7 Hz, *m*-C (Ph)], 130.01 (d, $^{4}J_{CP}$ = 3.1 Hz, *p*-C (Ph)], 132.25 [d, $^{2}J_{CP}$ = 8.4 Hz, *o*-C (Ph)], 133.47 [d, $^{1}J_{CP}$ = 83.2 Hz, *ipso*-C (Ph)]. − $^{29}Si\{^{1}H\}$ NMR (C_6D_6): δ = −1.72. − $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ = 16.98 ($^{2}J_{HgP}$ = 555.4 Hz). − $^{199}Hg\{^{1}H\}$ NMR (C_6D_6, 0.26 M, 298 K): δ = −507 ($^{2}J_{HgP}$ = 555.4 Hz). − $C_{27}H_{38}HgNPSi_2$ (664.3): calcd. C 48.82, H 5.77; found C 48.53, H 5.51.

$Ph_3P{=}C(iPr)HgN(SiMe_3)_2$ (**3c**): In a typical experiment 1.5 g of phosphorane **1b** (4.72 mmol) was treated with 2.46 g of **2** in 20 ml of toluene. Yield: 2.11 g (66%) of orange crystals, m.p. 93−96°C. − ^{1}H-NMR (C_6D_6): δ = 0.22 (s, 18H, $SiMe_3$), 1.30 (dd, 6H, $^{3}J_{HH}$ = 6.6, $^{4}J_{HP}$ = 1.2 Hz, Me), 2.86 (qd, 1H, $^{3}J_{HH}$ = 6.6, $^{3}J_{HP}$ = 22.0 Hz, CH), 6.85−7.10 [m, 9H, *m*/*p*-H (Ph)], 7.50−7.70 [m, 6H, *o*-H (Ph)]. − $^{13}C\{^{1}H\}$ NMR (C_6D_6): δ = 5.72 (s, $SiMe_3$), 30.02 (d, $^{2}J_{CP}$ = 6.0 Hz, CH), 33.30 (d, $^{3}J_{CP}$ = 12.2 Hz, Me), 61.45 (d, $^{1}J_{CP}$ = 81.3 Hz, PC_{ylide}), 128.79 [d, $^{3}J_{CP}$ = 9.8 Hz, *m*-C (Ph)], 130.97 [d, $^{4}J_{CP}$ = 2.7 Hz, *p*-C (Ph)], 133.21 [d, $^{2}J_{CP}$ = 8.8 Hz, *o*-C (Ph)], 134.82 [d, $^{1}J_{CP}$ = 82.5 Hz, *ipso*-C (Ph)]. − $^{29}Si\{^{1}H\}$ NMR (C_6D_6): δ = −1.69. − $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ = 15.97 ($^{2}J_{HgP}$ =

527.3 Hz). – ^{199}Hg{^{1}H} NMR (C_6D_6, 0.3 M, 298 K): δ = −484 ($^2J_{HgP}$ = 527.3 Hz). – $C_{28}H_{40}HgNPSi_2$ (678.4): calcd. C 49.58, H 5.94; found C 49.44, H 5.73.

$Ph_3P{=}C(Ph)HgN(SiMe_3)_2$ (**3d**): In a typical experiment 1.5 g of phosphorane **1b** (4.26 mmol) was treated with 2.22 g of **2** (4.26 mmol) in 20 ml of toluene. Yield: 2.05 g (67.5%) of yellow-orange crystals, m.p. 136–142°C. – ^{1}H NMR (C_6D_6): δ = 0.19 (s, 18H, $SiMe_3$), 6.59–6.57 [m, 1H, *p*-H (Ph)], 6.91–7.15 [m, 11H, *m*/*p*-H (Ph + PPh_3)], 7.18–7.24 [m, 2H, *o*-H (Ph)], 7.65–7.77 [m, 6H, *o*-H (PPh_3)]. – ^{13}C{^{1}H} NMR (C_6D_6): δ = 6.30 (s, $SiMe_3$), 61.33 (d, $^1J_{CP}$ = 91.3 Hz, PC_{ylide}), 118.41 [s, *p*-C (Ph)], 125.26 [d, $^3J_{CP}$ = 18.5 Hz, *o*-C (Ph)], 129.09 [m, *m*-C (Ph)], 129.74 [d, $^3J_{CP}$ = 11.5 Hz, *m*-C (PPh_3)], 132.26 [d, $^4J_{CP}$ = 2.7 Hz, *p*-C (PPh_3)], 132.35 [d, $^1J_{CP}$ = 85.1 Hz, *ipso*-C (PPh_3)], 134.46 [d, $^2J_{CP}$ = 9.0 Hz, *o*-C (PPh_3)], 148.80 [d, $^2J_{CP}$ = 5.7 Hz, *ipso*-C (Ph)]. – ^{29}Si{^{1}H} NMR (C_6D_6): δ = −0.75. – ^{31}P{^{1}H} NMR (C_6D_6): δ = 12.33 ($^2J_{HgP}$ = 546.9 Hz). – ^{199}Hg{^{1}H} NMR (C_6D_6, 0.23 M, 298 K): δ = −614 ($^2J_{HgP}$ = 546.9 Hz). – $C_{31}H_{38}HgNPSi_2$ (712.4): calcd. C 52.27, H 5.38; found C 52.89, H 5.26.

General Procedure for the Preparation of the Vinylmercury Compounds **4a–d**: The phosphoranes **3a–d** were synthesized as described above and used as isolated compounds or as prepared in solution without further purification. An equimolar amount of benzaldehyde was added with the help of a syringe to a cooled solution (−78°C) of **3a–d** in the solvent (with or without LiBr) given in Table 1. The reaction mixture was slowly warmed up to room temp. and stirred for 14 h. The solvent was removed in vacuo and the TPPO precepitated after the addition of *n*-hexane and cooling to −78°C for 3–4 h. Filtration gave a clear colorless or slightly yellow solution. All volatile components were evaporated in vacuo, and the residues were dissolved in C_6D_6 and characterized by NMR spectra.

(1-Methyl-2-phenylethenyl)mercury [Bis(trimethylsilyl)]amide (**4a**) *(Mixture of Z/E Isomers):* In a typical experiment 0.50 g of phosphorane **1a** (1.72 mmol) was treated with 0.90 g of **2** (1.72 mmol) to yield **3a**, and 0.18 g (1.72 mmol) of benzaldehyde was subsequently added to the reaction mixture at −78°C. The solution became *immediately* colorless. The isolated amount of TPPO was 0.40 g (85%) [in the presence of LiBr: 0.45 g (95%)]. Isolated yield of **4a**: 0.59 g (71.5%) of a slightly yellow, highly sensitive oil. – ^{1}H NMR (C_6D_6): δ = 0.24 [s, 36H, $SiMe_3$, (*Z*),(*E*)-**4a**], 1.87 [d, $^4J_{HH}$ = 1.75 Hz, 3H, Me, (*Z*)-**4a**], 1.90 [d, $^4J_{HH}$ = 1.92 Hz, 3H, Me, (*E*)-**4a**], 6.26 [m, 2H, =CH, (*Z*)/(*E*)-**4a**], 7.0–7.7 (m, 20H, aromat. H). – ^{199}Hg{^{1}H} NMR (C_6D_6, saturated solution, 298 K): δ = −856 [(*Z*)-**4a**], −949 [(*E*)-**4a**]; the *Z*/*E* ratios depend on the reaction conditions which are given in Table 1. – MS (FD): *m*/*z* 479 (cacld. $C_{15}H_{27}{}^{202}HgNSi_2$ 479.2).

(1-Ethyl-2-phenylethenyl)mercury [Bis(trimethylsilyl)]amide (**4b**) *(Mixture of Z/E Isomers):* In a typical experiment 0.50 g of phosphorane **1b** (1.64 mmol) was treated with 0.86 g of **2** (1.64 mmol) to yield **3b**, and 0.17 g (1.64 mmol) of benzaldehyde was added to the reaction mixture at −78°C. The solution became colorless at −40°C. The isolated amount of TPPO was 0.37 g (82%) [in the presence of LiBr: 0.44 g (97%)]. Isolated yield of **4b**: 0.61 g (75%) of a yellow, highly sensitive oil. – ^{1}H NMR (C_6D_6): δ = 0.17 [s, 36H, $SiMe_3$. (*Z*)/(*E*)-**4b**], 0.93 [t, 3H, $^3J_{HH}$ = 6.5 Hz, Me, (*E*)-**4b**], 1.03 [t, 3H, $^3J_{HH}$ = 6.27 Hz, Me, (*Z*)-**4b**], 2.29 [q, 2H, $-CH_2-$, $^3J_{HH}$ = 6.27 Hz, (*Z*)-**4b**], 2.44 [q, 2H, $-CH_2-$, $^3J_{HH}$ = 6.5 Hz, (*E*)-**4b**], 6.23 [m, 2H, =CH, (*Z*)/(*E*)-**4b**], 6.92–7.42 [m, 20H, aromat. H, (*Z*)/(*E*)-**4b**]. – ^{199}Hg{^{1}H} NMR (C_6D_6, saturated solution, 298 K): δ = −829 [(*Z*)-**4b**], −905 [(*E*)-**4b**]; the *Z*/*E* ratios depend on the reaction conditions which are given in Table 1.

(1-Isopropyl-2-phenylethenyl)mercury [Bis(trimethylsilyl)]amide (**4c**) *(Mixture of Z/E Isomers):* In a typical experiment 0.50 g of phosphorane **1c** (1.57 mmol) was treated with 0.82 g of **2** (1.57 mmol) to yield **3c**. Subsequently, 0.17 g (1.57 mmol) of benzaldehyde was added to the reaction mixture at −78°C. The solution became colorless at 0°C. The isolated amount of TPPO was 0.35 g (80%) [in the presence of LiBr: 0.42 g (96%)]. Isolated yield of **4c**: 0.63 g (78.5%) of a yellow, highly sensitive oil. – ^{1}H NMR (C_6D_6): δ = 0.21 [s, 18H, $SiMe_3$, (*Z*)-**4c**], 0.21 [s, 18H, $SiMe_3$, (*E*)-**4c**], 0.93 [d, 6H, $^3J_{HH}$ = 6.85 Hz, Me, (*E*)-**4c**], 1.05 [d, 6H, $^3J_{HH}$ = 6.54 Hz, Me, (*Z*)-**4c**], 2.76 [m, 1H, C*H*Me$_2$, (*Z*)-**4c**], 3.52 [m, 1H, C*H*Me$_2$, (*E*)-**4c**], 6.21 [m, 2H, =CH, (*Z*)/(*E*)-**4c**], 7.0–7.5 [m, 20H, aromat. H, (*Z*)/(*E*)-**4c**]. – ^{199}Hg{^{1}H} NMR (C_6D_6, saturated solution, 298 K): δ = −788 [(*Z*)-**4c**], −854 [(*E*)-**4c**]; the *Z*/*E* ratios depend on the reaction conditions which are given in Table 1.

(1,2-Diphenylethenyl)mercury [Bis(trimethylsilyl)]amide (**4d**) *(Mixture of Z/E Isomers):* In a typical experiment 0.5 g of phosphorane **1d** (1.42 mmol) was treated with 0.74 g of **2** (1.42 mmol) to yield **3d**, and 0.15 g (1.42 mmol) of benzaldehyde was added to the reaction mixture at −78°C. The solution became colorless at room temp. The isolated amount of TPPO was 0.28 g (70%) [in the presence of LiBr: 0.35 g (89%)]. Isolated yield of **4d**: 0.68 g (53%) of an orange, highly sensitive oil. – ^{1}H NMR (C_6D_6): δ = 0.20 [s, 36H, $SiMe_3$, (*Z*),(*E*)-**4d**], 6.45 [m, 2H, =CH, (*Z*)/(*E*)-**4d**], 6.90–7.70 [m, 40H, aromat. H, (*Z*)/(*E*)-**4d**]. – ^{199}Hg{[1H} NMR (C_6D_6, saturated, 298 K): δ = −879 [(*Z*)-**4d**], −1033 [(*E*)-**4d**]; the *Z*/*E* ratios depend on the reaction conditions which are given in Table 1.

General Procedure for Hydrolysis and Hydrolysis under Reductive Conditions of the Vinylmercury Amides **4a**, **4c**, **4d** *with Alkaline Solutions of* $NaBH_4$: The solutions of **4a–d** in *n*-hexane were cooled to 0°C and treated with a 1.5 molar amount of $NaBH_4$ in 3 M NaOH. Then solid NaCl was added, and the reaction mixture was warmed up to room temp. Filtration was necessary to remove precipitated HgO and, in the case of **4d**, elementary Hg. The organic layer was separated, the aqueous phase was extracted twice with diethyl ether, and the combined organic layers were dried with Na_2SO_4. Solvents were removed in vacuo, and the residue was chromatographed on SiO_2 (20 cm, 1.5 cm, eluent *n*-hexane/Et_2O, 10:1).

Bis(1-methyl-2-phenylethenyl)mercury (**7a**): [(*Z*,*Z*)/(*E*,*E*) isomer ratio: 24:76]: In a typical experiment **4a** was prepared as described above from 1.4 g (4.83 mmol) of **1a**, 2.52 g (4.83 mmol) of **2**, and 0.51 g (4.83 mmol) of benzaldehyde. Crude **4a** was dissolved in *n*-hexane and subsequently treated with 0.20 g of $NaBH_4$ (5.24 mmol) in 5 ml of 3 M NaOH. Yield: 0.84 g (80.0%) of a slightly yellow, air-stable solid; m.p. 47–49°C. – ^{1}H NMR ($CDCl_3$): δ = 2.21 [d, 3H, $^4J_{HH}$ = 1.47 Hz, Me, (*Z*)/(*Z*)-**7a**], 2.25 [d, 3H, $^4J_{HH}$ = 2.20, $^3J_{HHg}$ = 98.5 Hz, Me, (*E*)/(*E*)-**7a**], 6.42 [d, 1H, $^4J_{HH}$ = 1.47 Hz, =CH, (*Z*)/(*Z*)-**7a**], 6.49 [d, 1H, $^4J_{HH}$ = 2.20, $^3J_{HHg}$ = 98.5 Hz, =CH, (*E*)/(*E*)-**7a**], 7.12–7.76 (m, 20H, aromat. H). – ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 23.20 [Me, (*E*)/(*E*)-**7a**], 28.52 [Me, (*Z*)/(*Z*)-**7a**], 126.23, 126.27, 126.71, 126.79, 128.06, 128.70, 129.08, 129.12, 138.43, 141.73 (aromatic and olefinic C), 138.59 [=*C*Me, (*Z*)/(*Z*)-**7a**], 173.89 [=*C*Me, (*E*)/(*E*)-**7a**]. – ^{199}Hg{^{1}H} NMR ($CDCl_3$, 0.32 M, 298 K): δ = −708 [24%, (*Z*)/(*Z*)-**7a**], −824 [76%, (*E*)/(*E*)-**7a**]. – $C_{18}H_{18}Hg$ (434.9): calcd. C 49.71, H 4.17; found C 49.82, H 3.94.

Bis[(E)-1-isopropyl-2-phenylethenyl]mercury (**7c**): In a typical experiment crude **4c** [prepared from 1.5 g (4.72 mmol) of **1a**, 2.46 g (4.72 mmol) of **2**, 0.41 g of LiBr (4.72 mmol), and 0.50 g (4.72 mmol) of benzaldehyde, THF as solvent] in *n*-hexane was treated with 0.19 g of $NaBH_4$ (6.14 mmol) in 5 ml of 3 M NaOH. After chromatography the (*E*)/(*E*) isomer of **7c** was obtained in pure form; yield: 0.78 g (67%) of a colorless, air-stable solid; m.p. 80–82°C. – ^{1}H-NMR ($CDCl_3$): $\delta = 1.14$ (d, 6H, $^3J_{HH} = 6.45$ Hz, Me), 4.08 (sept, 1H, $^3J_{HH} = 6.45$ Hz, C*H*Me$_2$), 6.38 (m, 2H, =CH), 7.10–7.40 (m, 20H, aromat. C). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 25.34$ (Me), 126.36, 128.34, 128.96, 134.56, 139.12 (aromatic and olefinic C), 189.71 (=CHg). – $^{199}Hg\{^1H\}$ NMR ($CDCl_3$, 0.41 M, 298 K): $\delta = -561$. – $C_{22}H_{26}Hg$ (491.0): calcd. C 53.81, H 5.34; found C 52.93, H 5.24.

Stilbene (50:50 Mixture of (Z)/(E) isomers) (**8**): ^{1}H NMR ($CDCl_3$): $\delta = 6.47$ [s, 2H, =CH, (*Z*)], 6.98 [s, 2H, =CH, (*E*)], 7.00–7.45 [m, 20H, aromatic H, (*Z*)/(*E*)]. – $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 126.72$ [*o*-C, (*E*)], 127.24 [*p*-C, (*Z*)], 127.76 [*p*-C, (*E*)], 128.34 [*m*-C, (*Z*)], 128.80 [*m*-C, (*E*)], 128.93 [*o*-C, (*Z*)], 129.00 [=CH, (*E*)], 130.43 [=CH, (*Z*)], 137.45 [*ipso*-C Ph, (*Z*)], 137.58 [*ipso*-C Ph, (*E*)]. – NMR data were in accord with literature values[28].

X-Ray Single-Crystal Structure Determination of **3a**: Empirical formula $C_{26}H_{36}HgNPSi_2$; formula weight 650.30. Intensity data were collected with a Siemens-Stoe four-circle diffractometer [Mo-K_α radiation (0.71070 Å), ω scan]; temperature [K]: 293(2); crystal system: triclinic; space group $P\bar{1}$; unit cell dimensions [Å/°]: $a = 9.334(5)$, $b = 12.114(7)$, $c = 14.483(8)$, $\alpha = 101.46(4)$, $\beta = 105.38(4)$, $\gamma = 108.65(4)$; V [Å^3]: 1422.2(14); $Z = 2$; density (calculated) [g cm^{-3}]: 1.519; absorption coefficient [mm^{-1}]: 5.565; $F(000)$: 644; crystal size [mm]: 0.3 × 0.3 × 0.5; Θ range for data collection [°]: 1.50 to 25.00; index ranges: $-11 \leqslant h \leqslant 10$; $-14 \leqslant k \leqslant 14$; $0 \leqslant l \leqslant 17$; reflections collected: 4996; independent reflections: 4996 [$R(\mathrm{int}) = 0.0000$]; data/restraints/parameters: 4996/0/291; goodness-of-fit on F^2: 1.019; final indices: [$I > 2\sigma_I$] $R_1 = 0.0412$, $wR_2 = 0.1016$; R indices (all data): $R_1 = 0.0566$, $wR_2 = 0.1084$; extinction coefficient: 0.0067(6); largest diff. peak and hole [e Å^{-3}]: 1.616 and −1.557. An empirical absorption correction was applied ($0.441 < T < 0.744$). The structure was solved by the heavy atom method and refined by least-squares methods based on F^2 with all reflections. Anisotropic temperature factors for all non-hydrogen atoms were used. Hydrogen atoms were included in calculated positions or as part of a rigid group (CH_3) with common isotropic temperature factors. All calculations were performed by using the programs SHELXS 86[29] and SHELXL 93[30]. – Further details of the crystal-structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen (FRG) on quoting the depository number CSD-400704, the names of the authors, and the journal citation.

☆ Dedicated to Prof. *H. J. Bestmann*.

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