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# Structure of a Phosphazene–Aniline Compound

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## Abstract

The title compound [bis(trimethylphosphine phenylimide)–bis(aniline) (I), a 1:1 ratio of phosphazene and aniline molecules] was synthesized from the trapping of an *in situ* palladium nitrene complex with trimethylphosphine. Crystals of (I) consist of tetramers (two phosphazene and two aniline molecules) located at the 0,0,$\frac{1}{2}$) center of inversion in the space group $P\bar{1}$. The N atoms of the phosphazene molecules are involved in bifurcated hydrogen bonds with the amino H atoms of the aniline molecules.

## Comment

Tertiary alkyl and aryl phosphines have frequently been employed as trapping reagents for the isolation of reactive compounds and intermediates. One such family of compounds that is a product of these trapping reactions is phosphazenes. Phosphazenes are the nitrogen analogues of phosphorous ylides $R_3P{=}CR_2$. To produce a phosphazene from a tertiary phosphine, a nitrene source is required to generate the P=N double bond (Staudinger & Hauser, 1921):

$$R_3P + RN_3 \rightarrow R_3P{=}NR$$

Recently it was demonstrated that the phosphazene complex $Ph_3P{=}NPh$ was isolated from a zero-valent tungsten nitrene complex in the presence of $PPh_3$ (Sleiman, Mercer & McElwee-White, 1989).

Our interests involve the synthesis and characterization of nitrene complexes of palladium. When two equivalents of KNHPh were added to a solution of $[Pd(PMe_3)_3I][BFD_4]$ in THF at 195 K, compound (I) was isolated. Compound (I) was crystallized in pentane at 273 K, affording highly air and water sensitive light-brown needles of the title compound. It is likely that the generation of an *in situ* palladium nitrene complex in the presence of free $PMe_3$ is responsible for the formation of (I):

$$\begin{aligned} &2[Pd(PMe_3)_3I]^+ + 4NHPh^- \rightarrow \\ &\qquad 2\text{‘}(PMe_3)_2Pd{=}NPh\text{’} + 2NH_2Ph + 2PMe_3 \\ &\qquad\qquad\qquad \downarrow \\ &\qquad\qquad 2I + Pd + Pd(PMe_3)_4 \end{aligned}$$

Aniline is a by-product of the deprotonation of the second equivalent of KNHPh used to generate the intermediate nitrene complex. A $Pd^0$ species in the form of $Pd(PMe_3)_4$ was also produced in the reaction.

The thermal ellipsoid drawing (*SHELXTL-Plus*; Sheldrick, 1990) of the tetramer (two asymmetric units) with the atom-labeling scheme is given in Fig. 1. The tetramers are formed by hydrogen bonding between the amino H atoms and the N atoms of the phosphazene molecules. The hydrogen bonds have the following parameters: N11—H11*a* = 0.83 (3), H11*a*···N1*a* (related to N1 by the symmetry operation $-x$, $-y$, $1-z$) = 2.34 (3), N11···N1*a* = 3.152 (4) Å, N11—H11*a*···N1*a* = 166 (4)°, N11—H11*b* = 0.90 (4), H11*b*···N1 = 2.20 (4), N11···N1 = 3.092 (4) Å, N11—H11*b*···N1 = 174 (4)°.

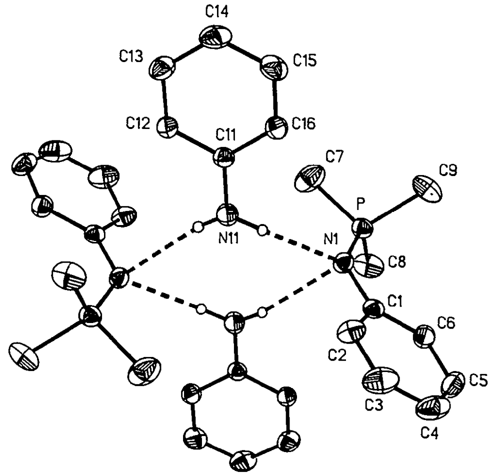

Fig. 1. Thermal ellipsoid drawing of two asymmetric units showing the tetramer, two phosphazene and two aniline molecules, held together by hydrogen bonding. Only the amino H atoms are included in the drawing. 50% probability ellipsoids are shown as well as the atom labels of the asymmetric unit.

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The phosphazene $Me_3P{=}NPh$ has been synthesized previously (Ostoja Starzewski & Dieck, 1979) and the $^{13}C[^1H]$ NMR spectrum of this compound is consistent with the $^{13}C[^1H]$ NMR spectrum of (I). All spectroscopic data were collected at 296 K in $C_6D_6$ on the Varian VXR-300 spectrometer. Proton and carbon chemical shifts were referenced to residual signals in the solvent and are reported relative to TMS. $^{31}P$ chemical shifts are reported relative to 85% $H_3PO_4$. $^1H$ NMR: $\delta$ 0.86 ($d$, $J_{P—H}$ = 12.8 Hz, 9H, $PMe_3$), 1.91 ($s$, 2H, $NH_2$), 6.36 ($d$, $J$ = 7.4 Hz, 2H), 6.71 ($t$, $J$ = 7.0 Hz, 1H), 6.86 ($t$, $J$ = 8.6 Hz, 1H), 6.95 ($d$, $J$ = 8.4 Hz, 2H), 7.07 ($t$, $J$ = 8.8 Hz, 2H), 7.28 ($t$, $J$ = 7.4 Hz, 2H). $^{13}C[^1H]$ NMR: $\delta$ 15.4 ($d$, $J_{P—C}$ = 67 Hz, $PMe_3$), 114.7, 116.6, 117.8, 122.5, 122.7, 129.1, 147.0. $^{31}P[^1H]$ NMR: $\delta$ 3.89.

## Experimental

### *Crystal data*

$C_9H_{14}NP.C_6H_7N$
$M_r$ = 260.31
Triclinic
$P\bar{1}$
$a$ = 8.276 (1) Å
$b$ = 8.819 (1) Å
$c$ = 12.045 (2) Å
$\alpha$ = 110.19 (1)°
$\beta$ = 92.61 (1)°
$\gamma$ = 106.84 (1)°
$V$ = 779.3 (2) Å$^3$
$Z$ = 2

$D_x$ = 1.109 Mg m$^{-3}$
Mo $K\alpha$ radiation
$\lambda$ = 0.71073 Å
Cell parameters from 50 reflections
$\theta$ = 20–22°
$\mu$ = 0.16 mm$^{-1}$
$T$ = 293 K
Needles
0.57 × 0.37 × 0.31 mm
Light brown

### *Data collection*

Siemens $P3m/V$ diffractometer
$\omega$ scans
Absorption correction: analytical
$T_{min}$ = 0.950, $T_{max}$ = 0.970
3854 measured reflections
3590 independent reflections
1842 observed reflections [$F > 6\sigma(F)$]

$R_{int}$ = 0.0112
$\theta_{max}$ = 27.5°
$h = 0 \rightarrow 10$
$k = -11 \rightarrow 11$
$l = -15 \rightarrow 15$
4 standard reflections monitored every 96 reflections
intensity variation: 5%

### *Refinement*

Refinement on $F$
Final $R$ = 0.0546
$wR$ = 0.0658
$S$ = 2.13
1842 reflections
238 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F) + 0.0004F]^2$

$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.24 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.28 e Å$^{-3}$
Atomic scattering factors from Cromer & Mann (1968) for non-H atoms and Stewart, Davidson & Simpson (1965) for H atoms

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å$^2$)

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| P | 0.32871 (12) | 0.20678 (12) | 0.74466 (8) | 0.0579 (4) |
| N1 | 0.1958 (3) | 0.2595 (3) | 0.6815 (2) | 0.0554 (13) |
| C1 | 0.1249 (4) | 0.3869 (4) | 0.7318 (3) | 0.0507 (14) |
| C2 | 0.0282 (5) | 0.4271 (6) | 0.6541 (4) | 0.074 (2) |
| C3 | −0.0444 (7) | 0.5525 (7) | 0.6960 (6) | 0.098 (3) |
| C4 | −0.0282 (7) | 0.6432 (6) | 0.8147 (7) | 0.101 (3) |
| C5 | 0.0621 (7) | 0.6061 (5) | 0.8928 (5) | 0.087 (3) |
| C6 | 0.1394 (5) | 0.4813 (5) | 0.8533 (3) | 0.065 (2) |
| C7 | 0.3752 (8) | 0.0430 (8) | 0.6322 (5) | 0.112 (4) |
| C8 | 0.2615 (6) | 0.1219 (8) | 0.8565 (5) | 0.093 (3) |
| C9 | 0.5287 (6) | 0.3711 (8) | 0.8148 (6) | 0.104 (3) |
| N11 | 0.1216 (4) | 0.0784 (5) | 0.4055 (3) | 0.073 (2) |
| C11 | 0.2424 (4) | 0.1132 (4) | 0.3352 (3) | 0.0490 (14) |
| C12 | 0.2252 (5) | 0.0036 (5) | 0.2175 (3) | 0.057 (2) |
| C13 | 0.3418 (5) | 0.0439 (5) | 0.1457 (3) | 0.071 (2) |
| C14 | 0.4771 (6) | 0.1912 (6) | 0.1900 (4) | 0.080 (2) |
| C15 | 0.4976 (5) | 0.3000 (5) | 0.3065 (4) | 0.078 (2) |
| C16 | 0.3805 (5) | 0.2617 (4) | 0.3784 (3) | 0.060 (2) |

Table 2. *Bond lengths* (Å) *and angles* (°) *for the non*-H *atoms of compound* (I)

| *A—B—C* | *A—B* | *A—B—C* |
|---|---|---|
| N1—P—C7 | 1.572 (3) | 106.7 (2) |
| N1—P—C8 | | 117.3 (2) |
| C7—P—C8 | 1.757 (6) | 105.5 (3) |
| C7—P—C9 | | 106.3 (3) |
| C8—P—C9 | 1.791 (7) | 104.7 (3) |
| C9—P—N1 | 1.787 (4) | 115.4 (3) |
| C1—N1—P | 1.385 (5) | 128.4 (2) |
| C11—N11 | 1.375 (5) | |
| C12—C11—N11 | | 121.0 (3) |
| C16—C11—N11 | | 120.8 (3) |

The $\omega$-scan width was symmetrical over 1.2° about the $K\alpha_{1,2}$ maximum and the background was offset 1.0 and −1.0 (in $\omega$) from the $K\alpha_{1,2}$ maximum. The scan speed was a variable 3–6° min$^{-1}$ (depending upon intensity). Anomalous-dispersion corrections were from Cromer & Liberman (1970). All H-atom coordinates were refined with isotropic thermal parameters and the isotropic thermal parameters of the methyl H atoms were fixed at 0.10 Å. Programs used: *SHELXTL-Plus* (Sheldrick, 1990) for cell refinement, data collection, data reduction, structure solution (direct methods) and molecular graphics; *SHELX76* (Sheldrick, 1976) for structure refinement (full-matrix least squares); *FUER* (S. B. Larson, personal communication) for geometric and parameter tables.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and bond distances and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71152 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1047]

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# Structures of *endo*- and *exo*-3-Acetoxy-2,4-diethoxy-6-(2-oxo-1,3-oxazolidin-3-ylcarbonyl)-3,4-dihydro-2*H*-pyran

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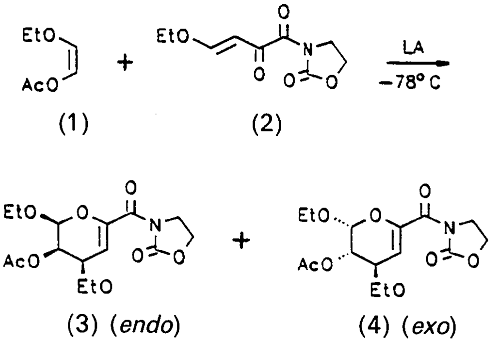
## Abstract

The crystal structures of $(\pm)$-$(2\beta,3\beta,4\beta)$- and $(\pm)$-$(2\alpha,3\alpha,4\beta)$-2,4-diethoxy-6-(2-oxo-1,3-oxazolidin-3-ylcarbonyl)-3,4-dihydro-2*H*-pyran-3-yl acetate (the *endo* compound with half a molecule of diethyl ether in the asymmetric unit) determined at 153 and 293 K, respectively, are reported. The two structures have similar bond lengths and angles and similar conformations.

## Comment

The *endo*/*exo* selectivity of the intermolecular Diels-Alder reaction of 4-ethoxy-1-(2-oxo-1,3-oxazolidin-3-yl)-3-butene-1,2-dione (2) with 2-ethoxyvinyl acetate (1) depends on the Lewis acid (LA) used. With $SnCl_4$, for example, a high *exo* selectivity is observed, whereas with $Me_2AlCl$, *endo* selectivity occurs. Details of the reaction have been published elsewhere (Tietze & Schneider, 1992; Schneider, 1992). In this paper we present the X-ray crystal structure of the *endo* product (3) and the *exo* product (4).



All bond lengths and angles are generally as expected. The conformations of the two structures are very similar. All H atoms were included in calculated positions and refined using a riding model. The ethoxy group in compound (3), O21 to C23, was found to be disordered. Two positions were refined with distance restraints for the 1-2 and 1-3 distances to an occupancy of

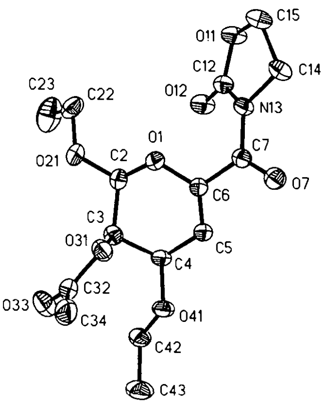


Fig. 1. Structure of compound (3) showing 50% probability displacement ellipsoids. The H atoms and the solvent molecule are omitted.

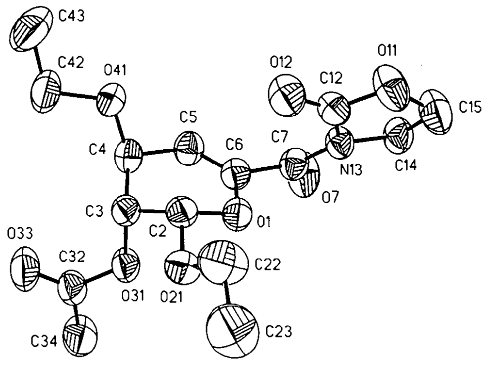


Fig. 2. Structure of compound (4) showing 50% probability displacement ellipsoids. The H atoms are omitted.

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