Bis(diphenylphosphanyl) Ligands

4,5-Bis(diphenylphosphanyl)-1,2,3-triazole and Its Conversion to 1,1,3,3,-Tetraphenyl-1,3-diphospha-2,4,5,6-tetraazapentalene

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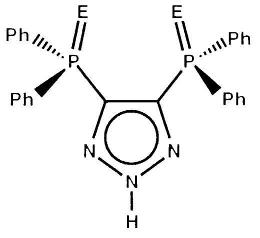
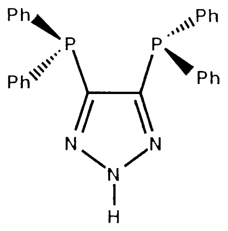
The novel ligand system, based on the anion of a 4,5-bis(diphenylphosphanyl)-1,2,3-triazole core, which may contain substituents, such as O, S, Se, NR or NAr, on the two phosphorus atoms, was reported for the case where the substituent was O.[1] This ligand was capable of coordinating in two different ways forming either a five- (O,N) or a seven-membered (O,O) chelate ring, depending on the chelated metal. More recently, the related $(L^{T\text{-}S2})^-$ ligand and some of its complexes were also described.[2] This general ligand type is abbreviated as $(L^{T\text{-}E2})^-$ in its anionic form, or as the free acid $HL^{T\text{-}E2}$, **1**, in which E is the particular heteroatom substituent on phosphorus, with HL^T being the abbreviation for the core molecule, the hitherto unknown 4,5-bis(diphenylphosphanyl)-1,2,3-triazole.[3]

Herein we report a) the synthesis of HL^T, **2**, the core molecule of the whole $HL^{T\text{-}E2}$ system, by deselenation of $HL^{T\text{-}Se2}$, and b) an unprecedented reaction of **2** with Me_3SiN_3, in the course of which **2** is transformed into the novel heterocycle, 1,1,3,3-tetraphenyl-1,3-diphospha-2,4,5,6-tetraazapentalene, **3**.



$HL^{T\text{-}E2}$ = **1**



HL^{T} = **2**

The reaction of $Ph_2PC{\equiv}CPPh_2$ with selenium formed the known diselenated derivative $Ph_2P(Se)C{\equiv}CP(Se)Ph_2$,[4,5] which reacted with NaN_3 to produce the sodium salt of the ligand, $NaL^{T\text{-}Se2}$, and this on acidification yielded the free acid, $HL^{T\text{-}Se2}$. The NaN_3 reaction required heating, and longer reaction times, than in the case of the oxo- and thio- analogues of $Ph_2P(Se)C{\equiv}CP(Se)Ph_2$, commensurate with the lower electron withdrawing power of the $-PPh_2{=}Se$ substituents in

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the series $-PPh_2{=}O > -PPh_2{=}S > -PPh_2{=}Se$ and, consequently, decreased activation of the triple bond. The new ligand was characterized as the triethylammonium salt, $HNEt_3L^{T\text{-}Se2}$, and its structure was determined by X-ray crystallography[6] and found to be similar to the previously reported $HNEt_3L^{T\text{-}S2}$.[3]

The free acid itself, $HL^{T\text{-}Se2}$ was an important starting material in the synthesis of the core heterocycle **2** [Eq. (1)].

$$HL^{T\text{-}Se2} + 2\,P(OEt)_3 \rightarrow \mathbf{2} + 2\,Se{=}P(OEt)_3 \qquad (1)$$

Treatment of $HL^{T\text{-}Se2}$ with $P(OEt)_3$ at room temperature resulted in double deselenation and the formation of HL^T, **2**, in good yield.[7] The related compounds $HL^{T\text{-}S2}$ and $HL^{T\text{-}O2}$ failed to react with $P(OEt)_3$ at room temperature, and under conditions designed to force the reaction gave rise only to 1N- and 2N-ethylated derivatives. The core molecule, **2**, has been structurally characterized (Figure 1). Its molecular dimensions in the triazole ring are similar to those found in $HL^{T\text{-}O2}$ and $HL^{T\text{-}S2}$ with the nonbonding distance between the two P atoms being 3.488 Å.

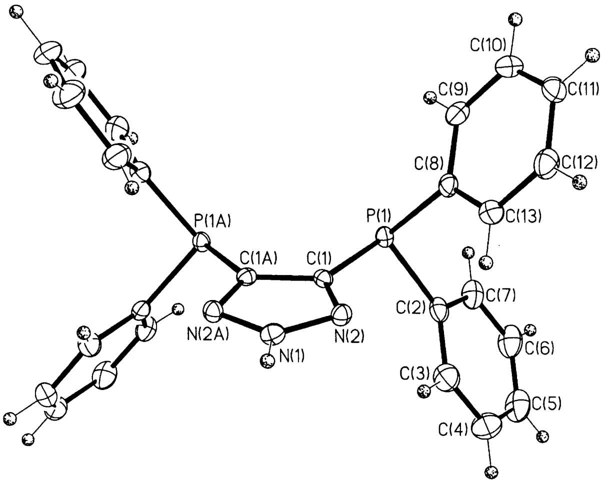
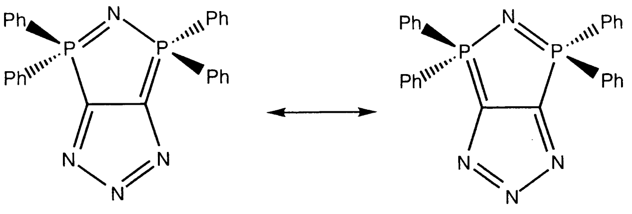


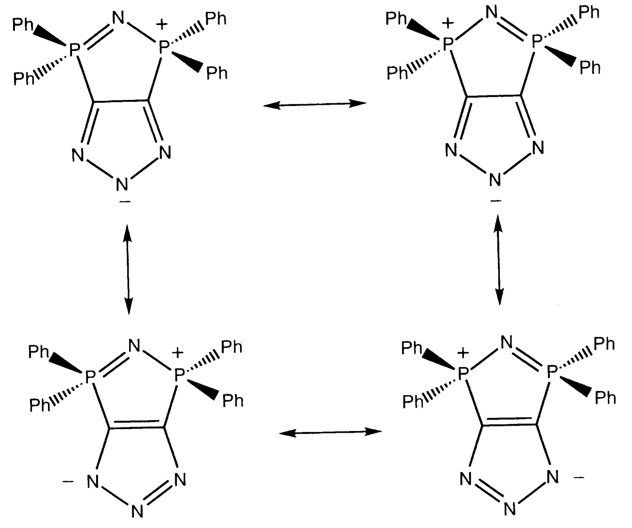
Figure 1. The X-ray crystal structure of HL^T, **2**. Selected bond distances [Å] and angles [°]: P(1)–C(1) 1.820(3); P(1)–C(8) 1.827(2); P(1)–C(2) 1.84393); C(1A)-C(1)-P(1) 124.95(9); C(1)-C(1A)-P(1A) 124.2(5).

Although, at first glance, **2** may be regarded as a simple chelating diphosphane, it has the special feature of containing the triazole proton, which upon removal by base will produce a chelating anionic diphosphane capable of forming neutral bisdiphosphane complexes $M[L^T]_2$ with divalent metals, and thus obviating the need for a counterion, ubiquitous in complexes with analogous neutral vicinal diphosphanes. Thus, **2** can chelate in two modes: as a neutral rigid diphosphane, or as an anionic rigid diphosphane, in each case forming identical five-membered chelate rings of C_{2v} symmetry. Both, the neutral HL^T and the anionic $(L^T)^-$ ligands are isoelctronic and isostructural. Such anionic chelating diphosphanes are unknown, although chelating diphosphanes forming six-membered rings as, for instance, $[Ph_2B(CH_2PPh_2)_2]^-$ and $[PhB(CH_2PPh_2)_3]^-$ were reported.[8,9]

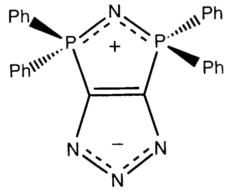
Compound **2** underwent an unprecedented "pseudo-Staudinger" reaction with Me_3SiN_3. Instead of the expected 1,2,3-triazole, which contains two $-PPh_2({=}NSiMe_3)$ substituents in the 4,5-positions, as is typical in the reaction of various diphosphane species with Me_3SiN_3,[10,11] we obtained a product that melts at high temperature, **3**, which was stable to air and moisture unlike the very sensitive known $RPPh_2({=}NSiMe_3)$ compounds.[12] Compound **3** also contained no $SiMe_3$ signals in the proton NMR spectrum, while its ^{31}P NMR had a single peak at $\delta = 22.3$ ppm, a region more characteristic of phosphorus(v) compounds. For instance, the ^{31}P resonances for $Et_3NH[L^{T\text{-}E2}]$ compounds were $\delta = 19.2$ ppm (E = O), 32.6 (E = S) and 22.2 ppm (E = Se), while HL^T had its ^{31}P resonance at $\delta = -36.1$ ppm. Structural characterization by X-ray crystallography showed **3** to be a novel molecule, 1,1,3,3-tetraphenyl-1,3-diphospha-2,4,5,6-tetraazapentalene, which belongs to the class of polyazapentalenes. Polyazapentalenes are known to be very stable due to the multiplicity of charge-separated zwitterionic forms that they can adopt,[13] and this seems to be the first example of a polyazapentalene containing phosphorus atoms incorporated into the pentalene ring system. In compound **3**, abbreviated as $L^{T\text{-}N}$, one can write canonical structures with alternating single and double bonds, in which both phosphorus atoms are in their highest, pentavalent oxidation state, as shown below.



One can also write numerous charge-separated structures:



As in all these charge-separated descriptions of the molecule the positive charge resides in the diphospha portion of the pentalene molecule, and the negative charge is



3 = L^{T-N}

distributed on the nitrogen atoms of the triazole-derived part, it might be appropriate to write the structure of **3** in delocalized zwitterionic form. Several simple cyclic salts, containing within a five-membered ring the moiety [$-P(Ph_2)P{=}N-P(Ph)_2-]^+$, associated with a separate bromide anion, were reported.[14]

The structure of **3** (Figure 2) is a molecule with C_{2v} symmetry, both phosphorus atoms being in identical environments. In agreement with this observation, the two equal P−N distances of 1.62 Å fell between the typical P=N and P−N values (1.59 and 1.68 Å, respectively), but closer to a P=N double bond. The triazolyl N(1)-N(2) and N(2)-N(3) bonds were slightly longer in **3** than in **2** (1.35 versus 1.33 Å), while the triazolyl C−N and C−C bonds lengths were essentially the same in **2** and **3** (1.35 and 1.40 Å, respectively). The linking of the two phosphorus atoms in **3** by the bridging nitrogen resulted in the shortening of the nonbonded P···P distance by 0.8 Å (2.696 Å in **3** versus 3.488 Å in **2**).

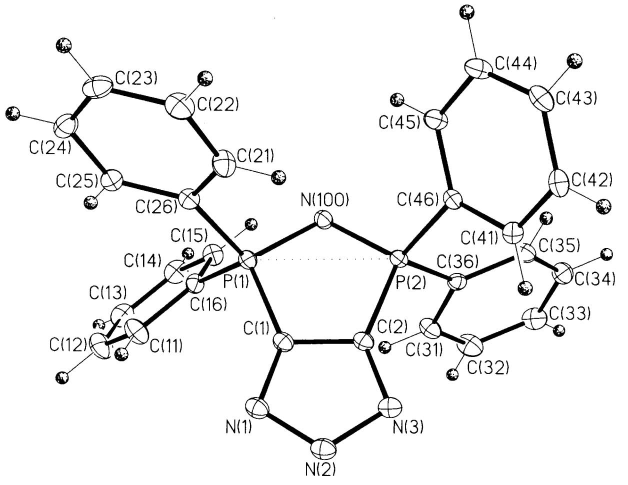


Figure 2. The X-ray crystal structure of L^{T-N}, **3**. Selected distances [Å] and angles [°]: P(1)−N(100) 1.6147(13); P(2)−N(100) 1.6101(13); P(1)−C(1) 1.7809(15); P(2)−C(2) 1.7779(15); C(1)−C(2) 1.394(2); N(100)-P(1)-C(1) 101.78(7); N(100)-P(2)-C(2) 101.75(7); P(1)-N(100)-P(2) 113.32(8).

Whatever the reaction mechanism of **2** with Me_3SiN_3 may be, the driving force for the formation of **3** appears to be the oxidation of both P atoms to the pentavalent state and the formation of the resonance-stabilized novel heterocycle, since in numerous other reactions of chelating diphosphanes with Me_3SiN_3 such oxidative bridging of the two phosphorus atoms was never observed. This net transfer of a single bridging nitrogen atom by Me_3SiN_3 in this "pseudo-Staudinger" reaction appears to be truly unprecedented.

In summary, we have prepared the selenium analogue of the known (L^{T-O2})$^-$ and (L^{T-S2})$^-$ ligands, (L^{T-Se2})$^-$, and converted its free acid to the core molecule of the whole HL^{T-E2} ligand system, HL^T, **2**. We have also shown that **2** reacts in unprecedented fashion with Me_3SiN_3, and is transformed into the stable novel heterocycle, 1,1,3,3-tetraphenyl-1,3-diphospha-2,4,5,6-tetraazapentalene, **3**. Various aspects of the coordination chemistry of the new ligands (L^{T-Se2})$^-$, (L^T)$^-$ and HL^T, are being investigated and will be reported in due course.

Experimental Section

All NMR spectra were determined in [D]chloroform, and the IR spectra in KBr. The deselenation reaction of HL^{T-Se2} and the reaction of HL^T with Me_3SiN_3 were carried out under nitrogen. Each of the products described was air-stable at ambient temperature.

HNEt$_3$L^{T-Se2}: A stirred slurry of $Ph_2P(Se)C{\equiv}CP(Se)Ph_2$ (19 g, 34 mol) and NaN_3 (2.5 g, 39 mol) in DMF (200 mL) was stirred and heated to 100 °C for until most of the NaN_3 had dissolved. The solution was decanted from a small amount of undissolved NaN_3, and poured slowly into HCl (1 L, 4 M). The precipitated crude HL^{T-Se2} was separated by filtration off and dried (yield 19.5 g, 96 %), and was used without further purification for the subsequent formation of **2**. HNEt$_3$L^{T-Se2} was obtained by stirring a sample of HL^{T-Se2} in methanol with excess triethylamine, followed by evaporation of this solution, and recrystallization of the product from acetonitrile. M.p. 196–198 °C, decomp; IR: $\tilde{\nu} = 3048$ (m), 2975 (m), 2621 (m), 2478 (m), 2358 (m), 1479 (s), 1436 (s), 1096 (s), 755 (s), 692 (s), 593 (s), 564 (s), 525 cm^{-1} (s). ^{1}H NMR: $\delta = 7.63$ (m, 8H, phenyl), 7.26 (m, 4H, phenyl), 7.16 (8H, phenyl), 3.00 (quartet, 6H, CH_2), 1.01 ppm (t, 9H, Me). ^{31}P NMR: $\delta = 22.2$ ppm, $J(^{31}P\text{-}^{77}Se)$ 361 Hz. Elemental analysis calcd (%) for $C_{32}H_{36}N_4P_2Se_2$: C 55.2, H 5.17, N 8.05; found: C 55.0, H 5.09, N 8.00.

2: An excess of $P(OEt)_3$ was added to a stirred slurry of HL^{T-Se2} (41.0 g, 68.9 mmol) in 100 mL chloroform, whereupon the solid dissolved within a few minutes. After 2 h the volatiles were removed by distillation, ultimately under high vacuum, and the crude **2** thus obtained (yield 29.8 g, 83.3 %), was recrystallized from acetonitrile; m.p. 137–138 °C; IR: $\tilde{\nu} = 3175$ (b), 3067 (s), 2998 (m), 1476 (s), 1430 (s), 1365 (m), 1092 (s), 1069 (s), 746 (vs), 692 (center of triplet, vs), 505 cm^{-1} (s). ^{1}H NMR: $\delta = 7.28$ ppm (unresolved m, phenyl); ^{31}P: $\delta = -36.1$ ppm. Elemental analysis calcd (%) for $C_{26}H_{21}N_3P_2$: C 71.4, H 4.81, N 9.69; found: C 71.5, H 4.97, N 9.55 %.

3: A mixture of **2** (12.8 g, 0.03 mol) and Me_3SiN_3 (10 mL, 0.08 mol) in 20 mL toluene was refluxed for 3 h, then the volatiles were removed by distillation, ultimately under high vacuum. The residue was washed with toluene/heptane and isolated by filtration. Crude **3** (yield 10.2 g, 77 %) was recrystallized from acetonitrile; m.p. 234–235 °C; IR: $\tilde{\nu} = 3051$ (s), 1557 (w), 1478 (m), 1434 (s), 1299 (m), 1118 (s), 746 (s), 727 (s), 697 (s), 570 (s), 509 cm^{-1} (s). ^{1}H NMR: $\delta = 7.45$ (four symmetrical m, 8H, *o*-H), 7.51 (m, 4H, *p*-H), 7.87 ppm (m, 8H, *m*-H); ^{31}P NMR: $\delta = 22.3$ ppm. Elemental analysis calcd (%) for $C_{26}H_{20}N_4P_2$: C 69.3, H 4.44, N 12.4; found C 69.5, H 4.53, N 12.2 %.

Crystal data for **2** and **3**: All data were collected by using Bruker CCD-equipped diffractometers, $Mo_{K''}$ radiation. For $C_{26}H_{21}N_3P_2$ (**2**), monoclinic, $C2/c$, $a = 16.3997(13)$, $b = 6.3423(5)$, $c = 22.3242(18)$ Å, $\beta = 104.5810(10)°$, $V = 2247.2(3)$ Å^3, $Z = 4$, $Z'' = 1$, $T = 173$ K, $\rho_{calc} = 1.293$ Mg m^{-3}. Of 4424 data collected, 1968 were independent. $R(F) = 5.38\,\%$, $wR(F^2) = 14.61\,\%$. There are two orientations for the molecule in an 83/17 ratio that are inversionally related. For $C_{26}H_{20}N_4P_2C{\cdot}0.5\,CH_3CN$ (**3**), monoclinic, $P2_1/c$, $a = 18.6594(11)$, $b = 13.9544(8)$, $c = 18.4924(11)$ Å, $\beta = 102.7540(10)°$, $V = 4696.3(5)$ Å3, $Z = 8$, $Z' = 2$, $T = 153$ K, $\rho_{calc} = 1.336$ Mg m^{-3}. The asymmetric unit contains two molecules of **3** and a molecule of acetonitrile disordered over two sites in approximately equal distribution. Of 53 778 data collected, 11 234 were independent. $R(F) = 4.58\,\%$, $wR(F^2) = 13.65\,\%$. For both molecules, all non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were treated as idealized contributions. All software is contained in libraries distributed by Bruker AXS (Madison, WI). CCDC-179388 (**2**) and CCDC-179389 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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