Diphosphanylketenimines: New Reagents for the Synthesis of Unique Phosphorus Heterocycles

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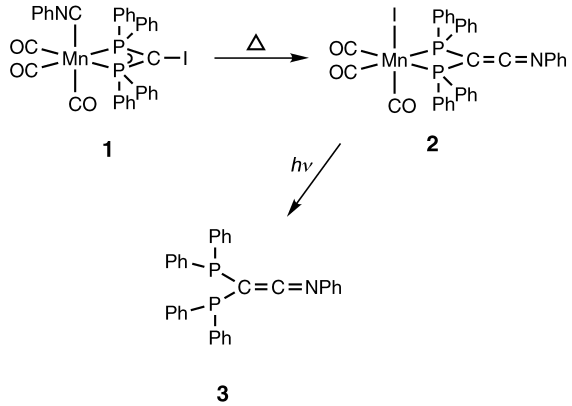
Abstract: Two consecutive [3+2] cycloaddition reactions of the diphosphanylketenimine $(PPh_2)_2C{=}C{=}NPh$ (**3**), involving the phosphanyl groups, with two equivalents of the electron-poor alkynes dimethyl acetylenedicarboxylate or methyl acetylenecarboxylate give rise to the formation of the bicyclic $1\lambda^5,3\lambda^5$-diphospholes **5a**,**b**, which contain a phosphorane unit with five carbon substituents attached to the phosphorus center. Compound **3** undergoes cyclodimerization by crystallization, affording the unsymmetrical dimer **6**, which is converted back to **3** by heating in toluene. Compound **6** can be oxidized stepwise on the three trivalent phosphorus atoms by treatment with H_2O_2 affording **7**, **9**, and the transient species **10**, which are transformed into their corresponding ketenimine monomers either spontaneously (**10**) or by heating in toluene (**7**, **9**). In this way, the compound $(O{=}PPh_2)(PPh_2)C{=}C{=}NPh$ (**8**) is quantitatively obtained. Compound **8** readily reacts with the alkynes $MeO_2CC{\equiv}C\text{-}CO_2Me$ and $MeO_2CC{\equiv}CH$, and with phenyl isocyanate and ethyl isothiocyanate through regiospecific [3+2] cycloaddition processes furnishing several λ^5-phosphole and λ^5-azaphosphole derivatives. Finally, the reaction of **8** with *N*-methylpropargylamine yields the new 2,3-dihydro-1,4-λ^5-azaphosphinine **15** through a cycloaddition process involving two functional groups from each molecule.

Keywords: cycloaddition · dimerization · ketenimines · phospholes · phosphorus heterocycles

Introduction

The reactivity of organic functional groups in cycloaddition reactions can be considerably enlarged by introducing phosphanyl substituents in the corresponding organic molecules, since the phosphorus atoms of the phosphanyl groups are frequently involved in the annelation processes. This is exemplified by a series of reactions of the electron-poor alkyne dimethyl acetylenedicarboxylate with phosphanyl-substituted carbodiimides,[1] azides,[2] nitrilimines[3] and diazoderivatives,[4] which afford a variety of new phosphorus containing heterocycles, such as $1,2\lambda^5$-azaphosphole, $1,2\lambda^5$-azaphosphete, $1,2,4,3\lambda^5$-triazaphosphinine and $1,2,4\lambda^5$-diazaphosphinine derivatives, respectively.

We have recently reported the first synthesis of the diphosphanylketenimine $(PPh_2)_2C{=}C{=}NPh$ (**3**), which is formally made from the coupling of the transient diphosphanylcarbene $[(PPh_2)_2C{:}]$ with phenyl isocyanide in the manganese(I) complex *fac*-$[Mn(CO)_3(CNPh)\{(PPh_2)_2CI\}]$ (**1**) (Scheme 1).[5] The new functionalized diphosphane **3** was liberated from the metallic fragment by irradiating with UV/Vis light. Compound **3** spontaneously undergoes cyclodimerization involving a phosphanyl residue upon crystallization.[6] This preliminary result prompted us to investigate the



Scheme 1. Synthesis of the diphosphanylketenimine **3**.

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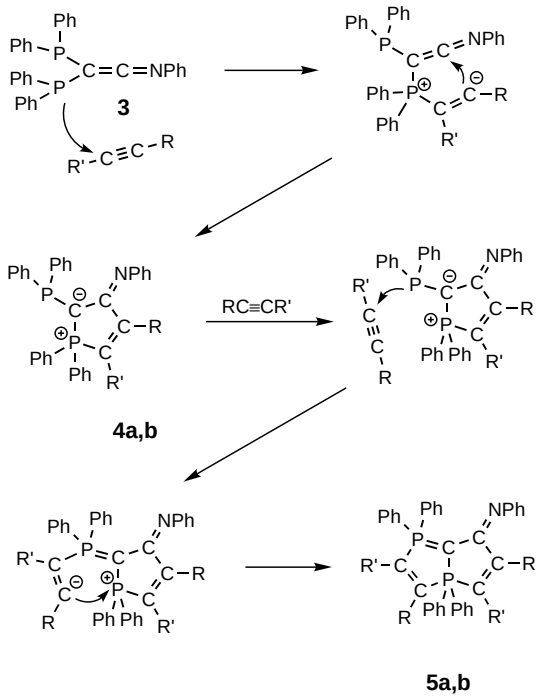
reactivity of **3** as a 1,3-dipole. Here we describe a detailed study of the reactions of **3** and its mono-oxide ($O{=}PPh_2$)(PPh_2)C=C=NPh (**8**) with several alkynes and heterocumulenes, which shows the value of these species in the synthesis of new phosphorus heterocycles. These results reveal diphosphanylketenimines as good examples of molecules that, being first generated on a metallic center, are then liberated from the metal and lastly transformed into more elaborate species.

Results and Discussion

Reactions of $(PPh_2)_2$C=C=NPh (3) with alkynes: The diphosphanylketenimine **3** reacted instantaneously at room temperature in CH_2Cl_2 with two equivalents of dimethyl acetylenedicarboxylate affording the bicyclic molecule **5a** (Scheme 2), which was isolated as a red solid. The reaction of **3** with the monosubstituted alkyne methyl acetylenecarboxylate proceeds similarly, yielding **5b**, although a longer reaction time (ca. 30 min) is required. With this terminal alkyne the reaction proved to be regiospecific, as only one of the four possible regioisomers is formed. Compounds **5a**,**b** are rare examples of $1\lambda^5,3\lambda^5$-diphospholes containing a phosphorane unit with five carbon substituents attached to a phosphorus center.[7, 8] Also of note is the presence of the endocyclic phosphonium ylide functionality, which is rather scarce in the chemistry of phospholes.[9] Both compounds were characterized by elemental analysis (C, H, N), spectroscopically and, in the case of **5a**, by single-crystal X-ray diffraction. The spectroscopic data for **5a**,**b** are in accordance with the proposed formulation of these compounds. Their $^{31}P\{^1H\}$ NMR spectra show two doublets for the two mutually coupled nonequivalent phosphorus atoms, one of them appearing at a remarkably high-field chemical shift (about $\delta = -80$), which is in keeping with the presence of a pentacoordinate phosphorus atom.[10] In the $^{13}C\{^1H\}$ NMR spectrum of **5a** the signal of the ylide carbon atom appears as a doublet of doublets in the expected high-field region ($\delta = 35.45$ ppm), with very large ^1J(P,C) coupling constants (183 and 136 Hz). The low-field signals ($\delta = 199.44$ and 170.29 ppm) are assigned to the olefinic carbon atoms directly bonded to the σ^5-P atom, whereas the resonances of the other two olefinic carbon atoms appear in the aromatic region ($\delta = 131.27$ and 117.19 ppm), all of them showing dd splitting. Other spectroscopic data for **5a**,**b** are detailed in the experimental section.



Scheme 2. Proposed mechanism for the formation of the bicyclic $1\lambda^5,3\lambda^5$-diphospholes **5a**,**b**. **5a**: $R = R' = CO_2Me$; **5b**: $R = CO_2Me$, $R' = H$.

The structure of **5a** was definitively established by X-ray crystallography. A view of the molecule together with a selection of bond lengths and angles is presented in Figure 1. The bicyclic skeleton is nearly planar and the pentacoordinate phosphorus atom P(1) is surrounded by five carbon atoms in a slightly distorted trigonal-bipyramidal coordination geometry. The C(1)–P(2) bond length (1.708(4) Å) is clearly shorter than a single bond and near to the range expected for a double bond between phosphorus and carbon, as in a phosphorus ylide fragment. Curiously, the C(1)–P(1) distance (1.729(4) Å) is much shorter than that of a single bond, indicating a strong interaction between the ylide carbon atom and the σ^5-P atom. In fact the rest of the P–C distances around P(1) are considerably longer, especially those in the axial positions (P(1)–C(5) 2.051(5), P(1)–C(4) 1.956(4) Å).

For **5b** crystals suitable for X-ray analysis could not be obtained. Furthermore, **5b** was not sufficiently stable in solution to allow a detailed spectroscopic study, therefore the proposed regioisomer assignment is tentative although the

Abstract in Spanish: *Dos procesos consecutivos de cicloadición [3 + 2] en la difosfanilcetenimina $(PPh_2)_2C{=}C{=}NPh$ (**3**), que involucran a los restos fosfanilo, con dos equivalentes de los alquinos electrónicamente pobres acetilendicarboxilato de dimetilo y acetilencarboxilato de metilo dan lugar a la formación de los λ^5-difosfoles bicíclicos **5a,b**, que contienen una unidad fosforano con cinco átomos de carbono unidos al fósforo. **3** experimenta una ciclo dimerización simplemente mediante cristalización generando el dímero **6**, que se convierte de nuevo en **3** por calentamiento en tolueno. **6** puede ser oxidado secuencialmente sobre los tres átomos de fósforo trivalentes mediante tratamiento con H_2O_2 formando **7**, **9**, y la especie transitoria **10**, que se transforman en sus correspondientes monómeros cetenimina ya sea espontáneamente (**10**) o mediante calentamiento en tolueno (**7**, **9**). De este modo se obtiene cuantitativamente el compuesto $(O{=}PPh_2)(PPh_2)$-C=C=NPh (**8**). **8** reacciona fácilmente con los alquinos $MeO_2CC{\equiv}CCO_2Me$ y $MeO_2CC{\equiv}CH$, y con fenil isocianato y etil isotiocianato, a través de procesos de cicloadición regioespecíficos [3+2] generando varios derivados del tipo λ^5-fosfol y λ^5-azafosfol. Finalmente, la reacción de **8** con N-Metilpropargilamina permite la obtención del nuevo derivado 2,3-dihidro-1,4-λ^5-azafosfinina **15**, a través de un proceso de cicloadición en el que participan dos grupos funcionales de cada molécula.*

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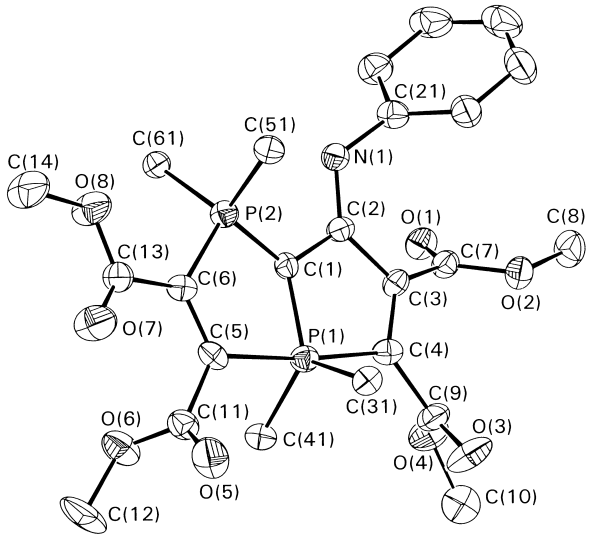

Figure 1. The molecular structure of **5a** (20% probability level). Phenyl groups attached to the phosphorus atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: P(1)–C(1) 1.729(4), P(1)–C(4) 1.956(4), P(1)–C(5) 2.051(5), P(1)–C(31) 1.815(5), P(1)–C(41) 1.812(5), P(2)–C(1) 1.708(4), P(2)–C(6) 1.791(4), P(2)–C(51) 1.789(5), P(2)–C(61) 1.795(4), C(2)–N(1) 1.310(5), C(1)–C(2) 1.450(5), C(2)–C(3) 1.483(5), C(3)–C(4) 1.341(5), C(5)–C(6) 1.344(6); C(1)-P(1)-C(4) 86.51(18), C(1)-P(1)-C(5) 87.70(18), C(1)-P(1)-C(31) 119.1(2), C(1)-P(1)-C(41) 123.1(2), C(41)-P(1)-C(31) 117.7(2), C(2)-C(1)-P(1) 116.0(3), C(2)-C(1)-P(2) 120.4(3), P(2)-C(1)-P(1) 121.3(2).

^{1}H NMR data agree with this formulation (see Experimental Section).

No reaction was found between **3** and nonactivated alkynes such as phenyl- or diphenylacetylene. These findings are in accord with a HOMO – LUMO interaction between **3** and the alkyne, the first acting as 1,3-dipole. In fact, the reactivity of these alkynes toward the ketenimine **3** correlates well with their LUMO energy, which is higher in PhC≡CH and PhC≡CPh than in the activated alkynes $MeO_2CC{\equiv}CH$ and $MeO_2CC{\equiv}CCO_2Me$.[11]

In line with all of the above, and with other reported cycloaddition reactions of alkynes with phosphanyl-substituted dipoles,[1, 4, 12, 13] a mechanism for the formation of **5a**,**b** is proposed in Scheme 2. First, nucleophilic attack of a phosphorus atom of **3** at the electron-poor alkyne followed by a 1,5-electrocyclization affords **4a**,**b**. Then, these phosphanyl-substituted phosphonium ylide intermediates behave as diphospha-1,3-dipoles toward a new molecule of alkyne, and the reaction proceeds as above to give **5a**,**b**. The species **4a**,**b** were not detected during the course of the reaction, even by using just one equivalent of the alkyne and working at low temperature. However, the isolation of the oxidized form of **4a**,**b** in a further experiment (compounds **12a**,**b**, see below) supported the proposed mechanism. Apparently **4a**,**b** are much more reactive as 1,3-dipoles than **3**. This behavior can arise from the contribution of the charge separation form to the phosphorus – carbon bond description in the phosphonium ylide fragment of **4a**,**b** (as emphasized in Scheme 2),[14] which enhances both the nucleophilicity of the phosphanyl substituent and the electrophilicity of the phosphonium residue. The mechanism proposed in Scheme 2 also accounts for the noteworthy regiospecificity of the reaction of **3** with $MeO_2CC{\equiv}CH$ to afford **5b**, as in both cycloaddition processes the nucleophilic attack of the phosphorus atom on the alkyne must take place on the unsubstituted carbon atom, either for electronic reasons[15] or for steric considerations.[16]

Synthesis of (O=PPh$_2$)(PPh$_2$)C=C=NPh (8): The presence of two phosphanyl groups in **3** renders this molecule highly reactive, but precludes the isolation of reaction intermediates as the above proposed **4a**,**b**. The involvement of both phosphorus atoms leads, in some cases, to intractable reaction mixtures, as occurs in the treatment of **3** with isocyanates and isothiocyanates. To better control the reactivity of these species we have prepared the monooxidized form of **3** (O=PPh$_2$)(PPh$_2$)C=C=NPh (**8**), which contains only one "active" phosphorus atom suitable for participation in cycloaddition reactions.

Compound **8** can not be prepared properly by direct oxidation of **3**. Thus, in the reaction of **3** with one equivalent of H_2O_2 a mixture of **8** and the dioxidized product (O=PPh$_2$)$_2$C=C=NPh (**11**), together with some unreacted starting material **3**, is obtained. Fortunately, the suitability of **3** to undergo reversible cyclic dimerization allowed us to obtain **8** in a pure form. As we have recently communicated,[6] the diphosphanylketenimine **3** dimerizes upon crystallization giving the unsymmetrical dimer **6** (Scheme 3), which quantitatively reverts to **3** on heating with toluene. The three trivalent phosphorus atoms in **6** can be selectively oxidized by treatment with one, two or three equivalents of H_2O_2 giving **7**, **9**, and the transient species **10**, respectively (Scheme 3). Heating of **7** and **9** under reflux in toluene for 10 min readily affords the corresponding monomers. For **10** this scission occurs instantaneously precluding its isolation. Very interestingly, compound **9** is the dimer of **8** so that the heating of the former quantitatively yields the target compound **8**. All the reactions above may be monitored very efficiently by ^{31}P{^{1}H} NMR spectroscopy. Thus a comparison between the resonances of **6** and those of **7** makes it evident that the first phosphorus atom to be oxidized is that bonded to the ylide carbon atom (P2 in Scheme 3) as its signal shifts strongly to low field on oxidation (see Experimental Section). For the same reason, the second oxidation apparently takes place on the phosphorus atom P3, although the change in the chemical shift of this signal is smaller in this case.

Reactivity of (O=PPh$_2$)(PPh$_2$)C=C=NPh (8): The reaction of **8** with the alkynes $MeO_2CC{\equiv}CCO_2Me$ and $MeO_2CC{\equiv}CH$ afforded the 3H-λ^5-phosphole derivatives **12a** and **12b**, respectively (Scheme 4). These are the oxidized forms of the intermediate species **4a**,**b** proposed in the formation of the bicyclic molecules **5a**,**b**, so that this result clearly supports the mechanism depicted in Scheme 2. It must be noted that 3H-λ^5-phospholes are very rarely encountered in the literature, and curiously they are stabilized by the presence of an imino substituent at C-3 as also seen in the case of **12a**,**b**.[1, 17].

Compound **8** also reacts with the heterocumulenes PhN=C=O and EtN=C=S. In both cases the [3+2] cycloaddition reaction takes place similarly to give the corresponding azaphospholenes **13** and **14** (Scheme 4). The IR spectra show the νCO (1634 cm^{-1}) and νCS (1262 cm^{-1}) absorptions for **13**

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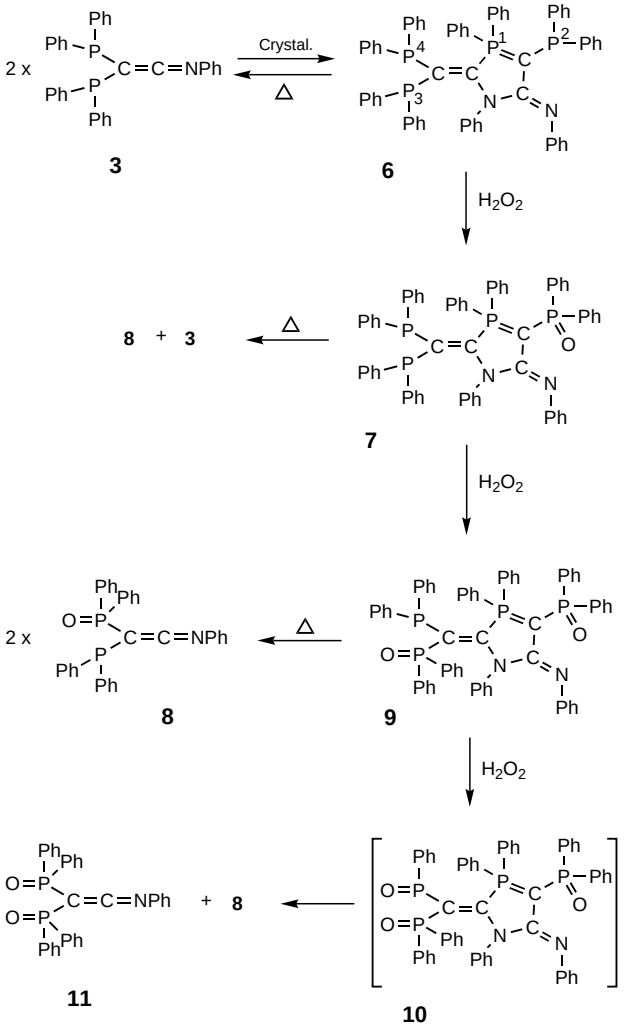
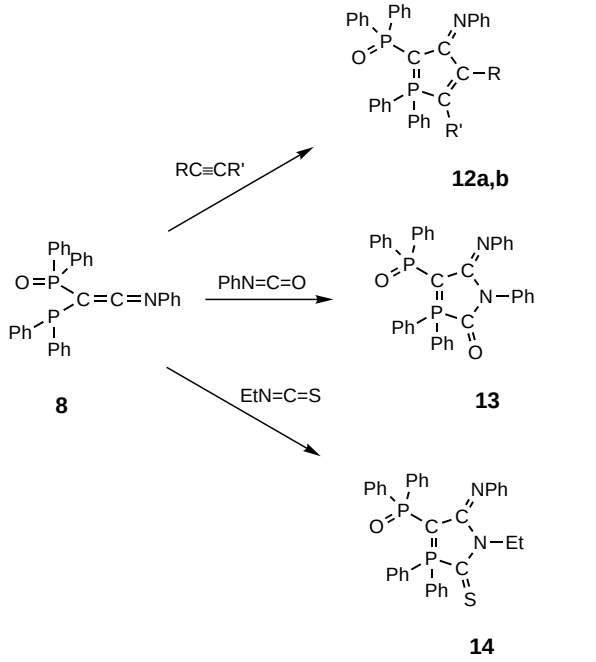


Scheme 3. Stepwise oxidation of the phosphorus atoms in the dimer **6** and formation of the corresponding monomers.



Scheme 4. [3+2] cycloaddition reactions of **8** with electron-poor alkynes and heterocumulenes. **12a**: R = R′ = CO_2Me; **12b**: R = CO_2Me, R′ = H.

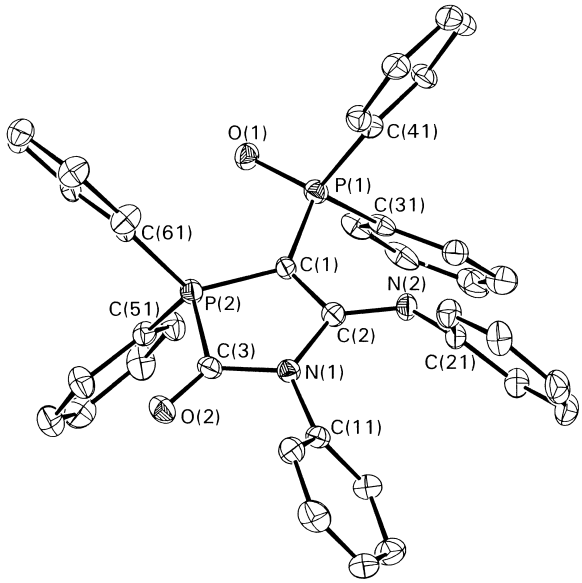
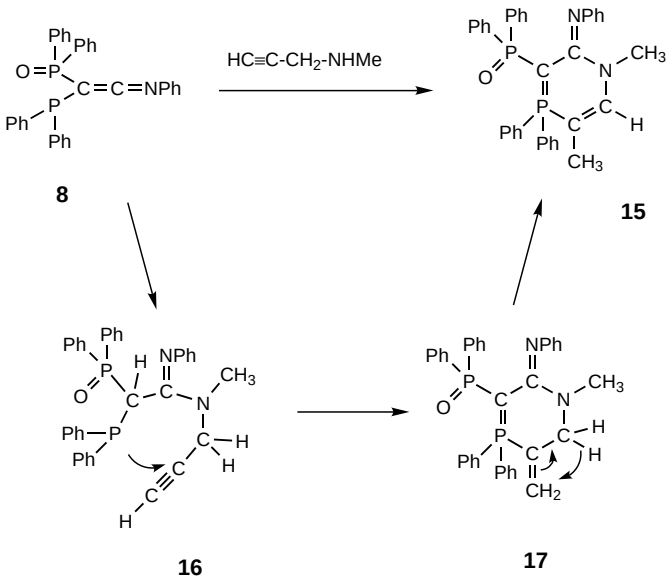


Figure 2. The molecular structure of **13** (20% probability level). Selected bond lengths [Å] and angles [°]: P(1)–O(1) 1.487(3), P(1)–C(1) 1.729(5), P(2)–C(1) 1.709(5), P(2)–C(3) 1.819(6), C(3)–O(2) 1.212(5), N(1)–C(3) 1.402(6), N(1)–C(2) 1.460(6), N(1)–C(11) 1.442(6), C(2)–N(2) 1.279(6), C(1)–C(2) 1.462(7); C(2)-C(1)-P(1) 126.9(4), C(2)-C(1)-P(2) 110.7(4), P(1)-C(1)-P(2) 122.1(3), C(2)-N(1)-C(3) 113.5(4), C(2)-N(1)-C(11) 127.0(4), C(3)-N(1)-C(11) 118.0(4).

and **14**, respectively, in addition to a band around 1600 cm^{-1} corresponding to the νCN vibration of the imino residue of both molecules. Furthermore, for **13** an X-ray diffraction study was carried out which confirmed the proposed structure for this molecule (Figure 2). The five-membered ring is essentially planar and the ylide carbon atom C1 is tightly bonded to both phosphorus atoms (C(1)–P(1) 1.729(5), C(1)–P(2) 1.709(5) Å). The N(1)–C(3) distance (1.402(6) Å), which is significantly shorter than a single bond, together with the almost planar coordination geometry around the endocyclic nitrogen atom N1 and with the C(3)–O(2) bond length (1.212(5) Å), which is slightly longer than that predicted for a double bond (1.17 Å),[18] suggest a strong π delocalization of the N(1) lone pair through the N(1)-C(3)-O(2) skeleton.

Compound **8** has also proved to be a promising substrate for the synthesis of six-membered phosphaheterocycles. Thus, the reaction of **8** with a doubly functionalized molecule such as HC≡CCH_2NHMe allowed us to obtain the new 2,3-dihydro-1,4-λ^5-azaphosphinine **15**.[19] A possible reaction pathway for the formation of this compound is shown in Scheme 5. First a nucleophilic addition of the amino group to the ketenimine moiety takes place to give the amidine derivative **16**, similar to that occurring in the reactions of amines with normal ketenimines.[20] Then **16** undergoes a formal *6-exo-dig* cyclization, prompted by the nucleophilic attack of the phosphane moiety to the alkyne residue followed by proton migration, affording the azaphosphaheterocycle **17**. This is finally transformed to **15** by a [1,3]-shift proton from the endocyclic methylene group to the exocyclic one. The ^1H NMR spectrum



Scheme 5. Proposed mechanism for the formation of the 2,3-dihydro-1,4-λ^5-azaphosphinine **15**.

of **15** shows the new methyl group as a doublet at $\delta = 1.65$ ppm ($^3J(P,H) = 12$ Hz), in addition to the N−Me signal which appears as a singlet at $\delta = 2.81$ ppm. The C−H proton gives a doublet ($^3J(P,H) = 29$ Hz) near to the aromatic region ($\delta =$ 6.75 ppm). The structure of **15** was also determined by X-ray crystallography (Figure 3). The atoms in the ring display an

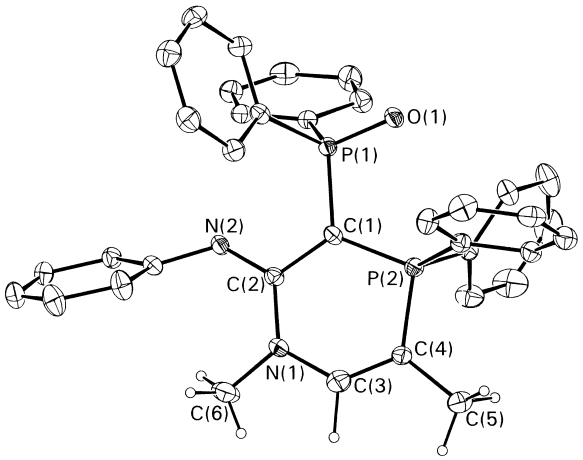


Figure 3. The molecular structure of **15** (20% probability level). Selected bond lengths [Å] and angles [°]: P(1)−O(1) 1.490(2), P(1)−C(1) 1.756(4), C(1)−P(2) 1.724(4), P(2)−C(4) 1.766(4), C(4)−C(3) 1.351(6), C(4)−C(5) 1.494(6), C(3)−N(1) 1.382(5), N(1)−C(6) 1.445(6), N(1)−C(2) 1.414(4), C(2)−N(2) 1.298(4), C(1)−C(2) 1.448(5); C(2)-C(1)-P(1) 119.9(3), C(2)-C(1)-P(2) 123.4(3), P(1)-C(1)-P(2) 115.65(19), C(2)-N(1)-C(3) 123.7(3), C(2)-N(1)-C(6) 122.0(3), C(3)-N(1)-C(6) 112.4(4).

essentially planar conformation with only the carbon atom C(1) slightly deviated from this plane (0.15 Å). All the bond lengths in the heterocycle are shorter than a single bond (see Figure 3), indicating the existence of some charge delocalization within the ring. Furthermore, the nitrogen atom N(1) adopts a nearly planar environment (N(1) lies 0.11 Å out of the C(2)-C(3)-C(6) plane), suggesting the involvement of the nitrogen lone pair in a π interaction with the neighboring atoms in the ring, so that this can complete a six π-electron system. Accordingly it can be inferred that compound **15** exhibits some degree of aromaticity.[21] This could be the driving force for the prototropic rearrangement occurring in the intermediate species **17** to afford **15**.

Conclusion

The diphosphanylketenimine $(PPh_2)_2C{=}C{=}NPh$ (**3**) and its mono-oxidized form $(O{=}PPh_2)(PPh_2)C{=}C{=}NPh$ (**8**) behave as 1,3-dipoles towards a variety of dipolarophiles such as alkynes, isocyanates and isothiocyanates, through formal [3+2] and [3+3] cycloaddition reactions involving the phosphanyl residues, allowing the synthesis of remarkable five- and six-membered phosphaheterocycles. Thus, it can be concluded that the presence of the phosphanyl substituents considerably modify the reactivity of **3** and **8** when compared with classical organic ketenimines, in agreement with that already observed by Regitz et al.[4] and Bertrand et al.[1] for other phosphanyl substituted organic functionalities.

Experimental Section

General: All reactions were carried out under a nitrogen atmosphere with the use of Schlenk techniques. Solvents were dried and purified by standard techniques and distilled under nitrogen prior to use. The IR spectra were measured with Perkin-Elmer FT 1720-X and Paragon 1000 spectrophotometers. The C, H and N analyses were performed on a Perkin-Elmer 240 B elemental analyzer. ^{1}H and ^{31}P NMR spectra were measured with Bruker AC-300 and AC-200 instruments. Chemical shifts are given in ppm, relative to internal $SiMe_4$ (^{1}H) or external 85% H_3PO_4 (^{31}P). The compounds **3**[5] and **6**[6] were prepared as described elsewhere. All other reagents were commercially obtained and used without further purification.

Compound 5a: Dimethyl acetylenedicarboxylate (40 µL, 0.32 mmol) was added to a solution of **3** (80 mg, 0.16 mmol) in CH_2Cl_2 (20 mL). The solution became instantaneously red. The mixture was stirred for 5 min and the solvent removed under vacuum. The brown residue was recrystallized from CH_2Cl_2/hexane to afford red crystals. Yield 85%. ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 7.99$ (dd, $^3J(P,H) = 14$, $^3J(H,H) = 7$ Hz, 4H; *ortho*-PPh), 6.8–7.8 (m, 19H; Ph), 6.52 (d, $^3J(H,H) = 7$ Hz, 2H; *ortho*-C=NPh), 3.50 (s, 3H; CH_3), 3.35 (s, 3H; CH_3), 3.27 (s, 3H; CH_3), 2.89 ppm (s, 3H; CH_3); ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2): $\delta = 8.97$ (d, $^2J(P,P) = 71$ Hz), −81.40 ppm (d, $^2J(P,P) = 71$ Hz); ^{13}C NMR (75.5 MHz, CD_2Cl_2): $\delta = 199.43$ (dd, $^1J(P,C) = 32$, $^2J(P,C) = 22$ Hz; PC=*C*P(σ^5)), 170.30 (dd, $^1J(P,C) = 25$, $^3J(P,C) = 4$ Hz; P*C*=CCN), 170.05 (dd, $^2J(P,C) = 14$, $^3J(P,C) = 10$ Hz; C=O), 169.15 (dd, $^3J(P,C) = 3$, $^4J(P,C) = 1$ Hz; C=O), 166.51 (dd, $^2J(P,C) = 6$, $^4J(P,C) = 2$ Hz; C=O), 162.41 (dd, $^2J(P,C) = 16$, $^3J(P,C) = 2$ Hz; C=O), 159.52 (dd, $^2J(P,C) = 23$, $^2J(P,C) = 13$ Hz; P_2CC=N), 151.86 (d, $^4J(P,C) = 5$ Hz; C=N*C*), 131.28 (dd, $^2J(P,C) = 12$, $^3J(P,C) = 7$ Hz; PC=*C*CN), 117.2 (dd, $^1J(P,C) = 93$, $^2J(P,C) = 6$ Hz; P*C*=CP(σ^5)), 52.60 (s; $1 \times CH_3$), 51.57 (s; $3 \times CH_3$), 35.40 ppm (dd, $^1J(P,C) = 183$, $^1J(P,C) = 136$ Hz; PCP); IR (Nujol): $\tilde{\nu} =$ 1720 (C=O), 1580 cm^{-1} (C=N); elemental analysis calcd (%) for $C_{44}H_{37}NO_8P_2$ (769.7): C 68.65, H 4.84, N 1.81; found: C 68.43, H 4.80, N 1.83.

Compound 5b: Methyl acetylenecarboxylate (28 µL, 0.32 mmol) was added to a solution of **3** (80 mg, 16 mmol) in CH_2Cl_2 (20 mL), and the resulting mixture was stirred for 30 min. The solvent was then evaporated to dryness under vacuum affording an orange residue which was washed with hexane. The resulting solid was dissolved in CH_2Cl_2 (1 mL) and then precipitated with hexane (10 mL). Yield 80%. ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 7.90$ (dd, $^3J(P,H) = 8$, $^3J(H,H) = 7$ Hz, 4H; *ortho*-PPh), 6.5–7.8 (21H; Ph), 6.68 (dd, $^2J(P,H) = 23$, $^3J(P,H) = 13$ Hz, 1H; PC(H)=C), 7.32 (dd, $^2J(P,H) = 14$, $^4J(P,H) = 4$ Hz, 1H; C(H)=CP), 3.20 (s, 3H; CH_3),

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2.80 ppm (s, 3H; CH_3); $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): $\delta = -0.50$ (d, $^2J(P,P) = 85$ Hz), -84.10 ppm (d, $^2J(P,P) = 85$ Hz); IR (Nujol): $\tilde{\nu} = 1718$ (C=O), 1586 cm^{-1} (C=N); elemental analysis calcd (%) for $C_{40}H_{33}NO_4P_2$ (653.6): C 73.50, H 5.09, N 2.14; found: C 72.43, H 4.82, N 1.91.

Compound 6: $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): $\delta = 28.50$ (ddd, $^2J(P1,P2) = 52$, $^3J(P1,P3) = 24$, $^3J(P1,P4) = 6$ Hz; P1), -22.83 (d, $^2J(P1,P2) = 52$ Hz; P2), 14.32 (dd, $^3J(P1,P3) = 24$, $^2J(P3,P4) = 4$ Hz; P3), 6.85 ppm (dd, $^3J(P1,P4) = 6$, $^2J(P3,P4) = 4$ Hz; P4); for the numbering of phosphorus atoms see Scheme 3.

Compound 7: Hydrogen peroxide (18 μL of a 30% aqueous solution, 0.16 mmol) was added to a solution of **6** (0.16 g, 0.16 mmol) in CH_2Cl_2 (50 mL). A slight darkening of the orange color of the solution was observed. Evaporation of the solvent to dryness under vacuum gave an oily residue, which was converted to an orange solid by washing with hexane. Yield: 90%. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): $\delta = 29.96$ (td, $^2J(P1,P2) = 31$, $^3J(P1,P3) = 12$, $^3J(P1,P4) = 6$ Hz; P1), 29.40 (dd, $^2J(P1,P2) = 31$, $^5J(P2,P3) = 6$ Hz; P2), 13.71 (dt, $^3J(P1,P3) = 12$, $^2J(P3,P4) = 6$, $^5J(P2,P3) = 6$ Hz; P3), 7.33 ppm (t, $^3J(P1,P4) = 6$, $^2J(P3,P4) = 6$ Hz; P4); for the numbering of phosphorus atoms see Scheme 3; elemental analysis calcd (%) for $C_{64}H_{50}N_2OP_4$ (987.0): C 77.88, H 5.10, N 2.83; found: C 77.25, H 4.98, N 2.90.

Compound 9: Hydrogen peroxide (18 μL of a 30% aqueous solution, 0.16 mmol) was added to a solution of **6** (80 mg, 0.08 mmol) in CH_2Cl_2 (30 mL). The solution instantly changed from orange to dark red. Evaporation of the solvent to dryness under vacuum gave an oily residue, which was converted to a red solid by washing with hexane. Yield: 90%. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): $\delta = 36.01$ (td, $^2J(P1,P2) = 31$, $^3J(P1,P3) = 31$, $^3J(P1,P4) = 21$ Hz; P1), 29.22 (d, $^2J(P1,P2) = 31$ Hz; P2), 19.26 (dd, $^3J(P1,P3) = 31$, $^2J(P3,P4) = 8$ Hz; P3), 0.45 ppm (dd, $^3J(P1,P4) = 21$, $^2J(P3,P4) = 8$ Hz; P4); for the numbering of phosphorus atoms see Scheme 3; elemental analysis calcd (%) for $C_{64}H_{50}N_2O_2P_4$ (1003.0): C 76.64, H 5.02, N 2.79; found: C 76.42, H 4.91, N 2.85.

Compound 8: A solution of **9** (80 mg, 0.08 mmol) in toluene (20 mL) was heated at the refluxing temperature for 10 min. Over this period it turned colorless. The solvent was evaporated to dryness affording a white solid, which was recrystallized from hexane. Yield 90%. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.78$ (dd, $^3J(P,H) = 11$, $^3J(H,H) = 7$ Hz, 4H; *ortho*-PPh), 6.5–7.5 ppm (21H; Ph); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): $\delta = 27.53$ (d, $^2J(P,P) = 87$ Hz; P=O), -14.80 ppm (d, $^2J(P,P) = 87$ Hz); ^{13}C NMR (75.5 MHz, CD_2Cl_2): $\delta = 168.33$ (dd, $^2J(P,C) = 10$, $^2J(P,C) = 3$ Hz; P_2C=*C*=N), 52.58 ppm (dd, $^1J(P,C) = 105$, $^1J(P,C) = 50$ Hz; P_2*C*=C=N); IR (CH_2Cl_2): $\tilde{\nu} = 2018$ cm^{-1} (C=C=N); elemental analysis calcd (%) for $C_{32}H_{25}NO_1P_2$ (501.5): C 76.64, H 5.02, N 2.79; found: C 76.55, H 5.01, N 2.65.

Compound 12a: Dimethyl acetylenedicarboxylate (21 μL, 0.17 mmol) was added to a solution of **8** (80 mg, 0.16 mmol) in CH_2Cl_2 (20 mL). After the mixture had been stirred for 5 min, the solvent was evaporated to dryness under vacuum to afford an oily residue. This was dissolved in CH_2Cl_2 (5 mL) and hexane (20 mL) was added to obtain a violet solid, which was recrystallized from CH_2Cl_2/hexane. Yield 85%. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.85$ (dd, $^3J(P,H) = 14$, $^3J(H,H) = 7$ Hz, 4H; *ortho*-PPh), 6.8–7.7 (19H, Ph), 6.55 (d, $^3J(H,H) = 7$ Hz, 2H; *ortho*-C=NPh), 3.10 (s, 3H; CH_3), 3.50 ppm (s, 3H; CH_3); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): $\delta = 31.60$ (d, $^2J(P,P) = 34$ Hz), 29.20 ppm (d, $^2J(P,P) = 34$ Hz); ^{13}C NMR (75.5 MHz, CD_2Cl_2): $\delta = 164.83$ (d, $^2J(P,C) = 17$ Hz; C=O), 161.81 (d, $^3J(P,C) = 4$ Hz; C=O), 150.58 (d, $^4J(P,C) = 4$ Hz; C=N*C*), 53.14 (s; CH_3), 52.58 (s; CH_3), 31.08 ppm (dd, $^1J(P,C) = 169$, $^1J(P,C) = 24$ Hz; P*C*P); IR (Nujol): $\tilde{\nu} = 1751$ (C=O), 1733 (C=O), 1579 cm^{-1} (C=N); elemental analysis calcd (%) for $C_{38}H_{31}NO_5P_2$ (643.6): C 70.91, H 4.85, N 2.18; found: C 70.63, H 4.79, N 2.16.

Compound 12b: This compound was prepared similarly to **12a** by treating **8** (50 mg, 0.1 mmol) with methyl acetylenecarboxylate (11 μL, 0.12 mmol) in CH_2Cl_2 for 1 h. Yield 85%. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 6.7–8.2$ (25H; Ph), 6.63 (dd, $^2J(P,H) = 19$ Hz, $^4J(P,H) = 3$ Hz, 1H; C=CH), 3.09 ppm (s, 3H; CH_3); $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): $\delta = 29.76$ (d, $^2J(P,P) = 38$ Hz), 28.40 ppm (d, $^2J(P,P) = 38$ Hz); IR(Nujol): $\tilde{\nu} = 1733$ (C=O), 1554 cm^{-1} (C=N); elemental analysis calcd (%) for $C_{36}H_{29}NO_3P_2$ (585.6): C 73.84, H 4.99, N 2.39; found: C 73.37, H 4.75, N 2.19.

Compound 13: A mixture of compound **8** (80 mg, 0.16 mmol) and phenyl isocyanate (87 μL, 0.80 mmol) was heated in refluxing toluene (20 mL) for 10 min. The solvent was then evaporated to dryness under vacuum and the remaining oil was washed with hexane (3 × 10 mL) affording a yellow solid. This was recrystallized from CH_2Cl_2/hexane. Yield 75%. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): $\delta = 28.90$ (d, $^2J(P,P) = 24$ Hz), 4.96 ppm (d, $^2J(P,P) = 24$ Hz); ^{13}C NMR (75.5 MHz, CD_2Cl_2): $\delta = 170.51$ (dd, $^1J(P,C) = 94$, $^3J(P,C) = 12$ Hz; C=O), 147.10 (dd, $^2J(P,C) = 14$, $^2J(P,C) = 7$ Hz; C=N), 148.07 (d, $^4J(P,C) = 4$ Hz; C=N*C*), 136.02 (d, $^4J(P,C) = 4$ Hz; C_2N*C*), 41,44 ppm (dd, $^1J(P,C) = 131$ Hz, $^1J(P,C) = 97$ Hz; PCP); IR (KBr): $\tilde{\nu} = 1634$ (C=O), 1587 cm^{-1} (C=N); elemental analysis calcd (%) for $C_{39}H_{30}N_2O_2P_2$ (620.6): C 75.48, H 4.87, N 4.51; found: C 75.76, H 4.65, N 4.53.

Compound 14: A mixture of compound **8** (50 mg, 0.1 mmol) and ethyl isothiocyanate (87 μL, 1 mmol) was heated in refluxing toluene (20 mL) for 3 h. The solvent was evaporated to dryness and the remaining residue washed with hexane affording an orange solid which was recrystallized from CH_2Cl_2/Hexane. Yield 70%. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 6.7–7.7$ (23H; Ph), 6.40 (d, $^3J(H,H) = 6$ Hz, 2H; *ortho*-NPh), 4.30 (q, $^3J(H,H) = 6$ Hz, 2H; CH_2N), 1.20 ppm (t, $^3J(H,H) = 6$ Hz, 3H; CH_3); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): $\delta = 25.02$ (d, $^2J(P,P) = 25$ Hz), 20.50 ppm (d, $^2J(P,P) = 25$ Hz); ^{13}C NMR (75.5 MHz, CD_2Cl_2): $\delta = 192.18$ (dd, $^1J(P,C) = 74$, $^3J(P,C) = 8$ Hz; C=S), 151.60 (dd, $^2J(P,C) = 16$, $^2J(P,C) = 10$ Hz; C=N), 147.67 (s; C=N*C*), 41.84 (d, $^3J(P,C) = 5$ Hz; CH_2), 40,72 (dd, $^1J(P,C) = 124$ Hz, $^1J(P,C) = 87$ Hz; P*C*P), 12.30 ppm (s; CH_3); IR(KBr): $\tilde{\nu} = 1631$ (C=N), 1262 cm^{-1} (C=S); elemental analysis calcd (%) for $C_{35}H_{30}N_2OP_2S$ (588.6): C 71.42, H 5.14, N 4.76; found: C 71.72, H 4.82, N 4.52.

Compound 15: A mixture of compound **8** (50 mg, 0.1 mmol) and *N*-methylpropargylamine (17 μL, 0.2 mmol) was heated in refluxing toluene (20 mL) for 10 min. Then the solution was concentrated to 5 mL under vacuum. Addition of hexane (10 mL) resulted in the formation of a white solid. Yield 70%. Crystals of **15** suitable for X-ray analysis were obtained by recrystallization from CH_2Cl_2/hexane. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 6.75$ (d, $^3J(P,H) = 29$ Hz, 1H; C=CH), 2.81 (s, 3H; NCH_3), 1.65 ppm (d, $^3J(P,H) = 12$ Hz, 3H; CCH_3); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): $\delta = 36.22$ (d, $^2J(P,P) = 27$ Hz), 9.27 ppm (d, $^2J(P,P) = 27$ Hz); ^{13}C NMR (75.5 MHz, CD_2Cl_2): $\delta = 150.10$ (dd, $^2J(P,C) = 12$, $^2J(P,C) = 5$ Hz; C=N), 147.47 (d, $^4J(P,C) = 5$ Hz; C=N*C*), 86.32 (dd, $^1J(P,C) = 82$ Hz, $^1J(P,C) = 7$ Hz; P*C*P), 42.87 (s; NCH_3), 15.20 ppm (d, $^2J(P,C) = 6$ Hz; C*C*CH_3); elemental analysis calcd (%) for $C_{36}H_{32}N_2OP_2$ (570.6): C 75.78, H 5.65, N 4.91; found: C 75.56, H 5.68, N 5.23.

X-ray crystallographic study: Data collection was carried out on an Enraf–Nonius KappaCCD diffractometer for **5a**, **13** and **15**. Graphite-monochromated $Cu_{K\alpha}$ radiation ($\lambda = 1.54184$ Å)$_\alpha$ was used. The structures were solved by direct methods, and refined by full-matrix least-squares methods with the following program packages: DIRDIF92[22] and SHELXL-97[23]. Relevant crystallographic data and details of the refinement for the three structures are given in Table 1. CCDC-180291 (**5a**), CCDC-180292 (**13**),

Table 1. Crystallographic data for compounds **5a**, **13**, and **15**.

	5a	**13**	**15**
formula	$C_{44}H_{37}NO_8P_2$	$C_{39}H_{30}N_2O_2P_2$	$C_{36}H_{32}N_2OP_2$
formula weight	769.69	620.59	570.58
temperature [K]	200	200	200
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	$P2_1/c$
a [Å]	12.2664(13)	16.5595(10)	13.0516(8)
b [Å]	18.4425(12)	8.5353(4)	15.1368(10)
c [Å]	18.0416(9)	22.3717(14)	16.3258(9)
α [°]	90	90	90
β [°]	106.1850(10)	91.383(3)	112.330(4)
γ [°]	90	90	90
V [Å^3]	3919.7(5)	3160.2(3)	2983.4(3)
Z	4	4	4
ρ_{calcd} [g cm^{-3}]	1.304	1.304	1.270
μ[mm^{-1}]	1.464	1.549	1.564
θ range [°]	3.50–68.17	2.67–63.65	3.66–69.77
reflections collected	6232	4208	9725
independent reflections	6232	4208	5546
goodness-of-fit on F^2	1.048	0.931	1.077
final R indices [$I > 2\sigma(I)$]; $R1$, $wR2$	0.0709, 0.1806	0.0629, 0.1299	0.0590, 0.1390
R indices (all data); $R1$, $wR2$	0.1098, 0.2447	0.1346, 0.1636	0.1008, 0.1694

and CCDC-180293 (**15**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at 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 e-mail: deposit@ccdc.cam.ac.uk).

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