

From a terminal (*cis*-2-butene-1,4-diyl-1,4-diphosphinidene) complex to some new diphosphorus bicycles[☆]

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Abstract

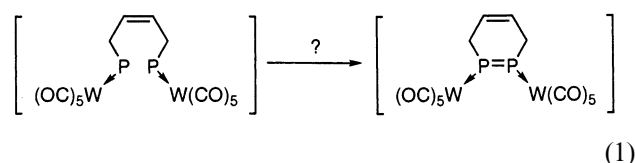
The reaction of the transient [*cis*-2-butene-1,4-diyl-1,4-diphosphinidene]decacarbonylditungsten complex (**3**) as generated from the appropriate 7-phosphanorbornadiene precursor (**2**) at 60°C in the presence of CuCl as a catalyst with 3-hexyne, 2,3-dimethylbutadiene and [phenyl(methoxy)carbene]pentacarbonyltungsten yields the products **5**, **7** and **8**. These products formally result from the [2 + 2], [4 + 2] and [1 + 2] cycloadditions of the reagents with the P=P double bond of the [3,6-dihydro-1,2-diphosphinine]decacarbonylditungsten. However, a mechanism involving a monocondensation of the reagent onto one P of the bis-phosphinidene, followed by the insertion of the second P into the monophosphorus heterocycles thus formed is favored. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: 1,6-Diphosphabicyclo[4,n,0] compounds; P-insertion; Phosphinidene; Carbene complex

1. Introduction

For some time now, transient electrophilic terminal phosphinidene complexes [RP → M] [M = Cr, Mo, W(CO)₅] have been developed into a highly efficient tool for the synthesis of P–C heterocycles from alkenes, alkynes, dienes, etc. [1]. As a next logical step toward more elaborate structures, it was interesting to investigate the chemistry of α,ω-alkanediyl diphosphinidene complexes with the hope of observing intramolecular condensation reactions of some practical interest. A preliminary work concerning 1,2-ethanediphosphinidene complexes was reported some years ago [2]. In that case, both phosphorus functionalities react normally and independently with external reagents. In order to favor the intramolecular interactions between

the two reactive termini, we decided to investigate the case of a (*cis*-2-butene-1,4-diyl)diphosphinidene complex. Due to the favorable geometry, the intermediate formation of a 3,6-dihydro-1,2-diphosphinine ring could be envisaged in that case (Eq. (1)). The formation of P=P double bonds by dimerization of terminal phosphinidene complexes is indeed well documented [3]. We report here on the results of this study.



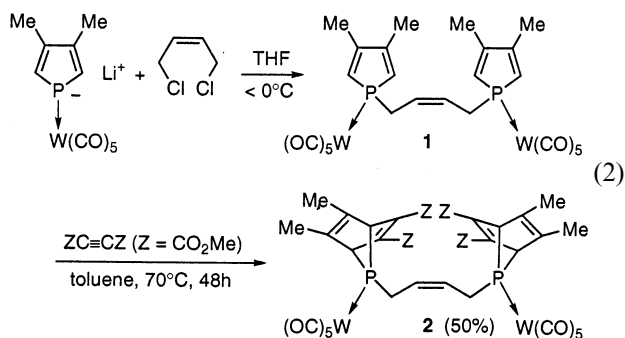
2. Results and discussion

The appropriate 7-phosphanorbornadiene precursor **2** was prepared as usual (Eq. (2)).

[☆] Dedicated to Professor Alan Cowley for his 65th birthday.

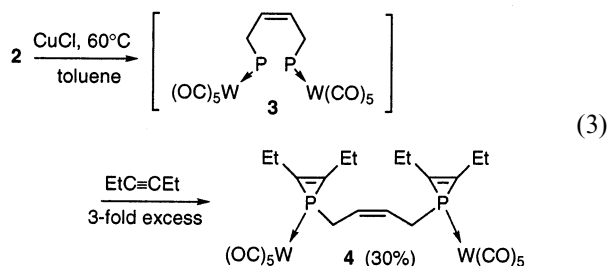
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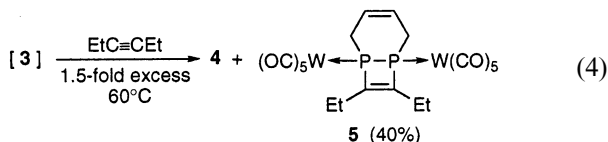


In spite of the bulkiness associated with the P–CH₂–CH=CH–CH₂–P bridge, the cycloaddition takes place on the phosphole side opposite to the tungsten complexing group as shown by the couplings of Me–C₅, Me–C₆, MeO₂C–C₂, MeO₂C–C₃ with phosphorus: $\delta(\text{C}_5, \text{C}_6)$ 139.02, $^2J(\text{C}–\text{P}) = 16.8$ Hz; $\delta(\text{C}_2, \text{C}_3)$ 145.57, $^2J(\text{C}–\text{P})$ ca. 0 Hz. The $^2J(\text{C}–\text{P})$ are indeed highly dependent on the C–C–P–W dihedral angles and these data correspond closely to those of the structurally characterized 7-phosphanorbornadiene complexes [4].

All our attempts to generate the bis-phosphinidene **3** from **2** by thermal decomposition failed to give anything other than polymeric products. On the contrary, trapping experiments with various unsaturated substrates gave satisfactory results. The reaction with 3-hexyne in large excess gives the corresponding bis-phosphirene complex **4** (Eq. (3)).

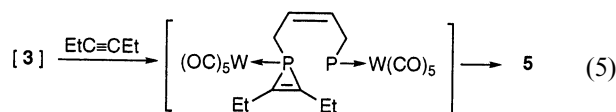


The bis-phosphirene is characterized by its high-field ^{31}P resonance at -158 (CDCl_3). Together with the fact that it is impossible to get well-defined products during the thermal decomposition of **2**, this result tends to demonstrate that the formation of the 3,6-dihydro-1,2-diphosphinane ring from **3** by P=P coupling is not a highly favored process. A more exciting result was obtained when **3** was generated in the presence of a limited amount of 3-hexyne. Together with the bis-phosphirene **4**, another product **5** was formed (Eq. (4)) which does not incorporate a three-membered ring as shown by its ^{31}P resonance at 7.5 (CDCl_3).



The mass spectrum indicates that **5** results from the addition of one molecule of hexyne to one molecule of

3 (m/z 846 for ^{184}W). The structure was solved by X-ray analysis (Fig. 1). It shows the formation of a four-membered 1,2-dihydro-1,2-diphosphete ring. The junction between the six- and the four-membered rings has a *cis* stereochemistry. The P–P bond length is normal at 2.224(2) Å. The geometry of the four-membered ring is very close to that reported previously for a *cis*-1,2-dihydro-1,2-diphosphete complex [5]. A priori, two mechanisms can account for the formation of **5**. The first one would involve a P=P coupling followed by a [2 + 2] cycloaddition between the P=P double bond and the alkyne. Such [2 + 2] cycloadditions have already been described previously [3b]. The formation of **4** in the same reaction suggests a more likely pathway involving the initial formation of a mono-phosphirene followed by the intramolecular insertion of the phosphinidene into the phosphirene (Eq. (5)). Such an insertion has also some precedent in the literature [5].



We then investigated the reaction of **2** with 2,3-dimethylbutadiene. The reaction of terminal phosphinidene complexes with conjugated dienes is known to give 2-vinylphosphirane complexes which rearrange upon heating to the corresponding phospholenes [6]. In the case of **2**, the reaction produces two isomeric bis-(vinylphosphirane) complexes **6a,b** in minor quantities, but the main product **7** is not a bis-phospholene complex (Eq. (6)).

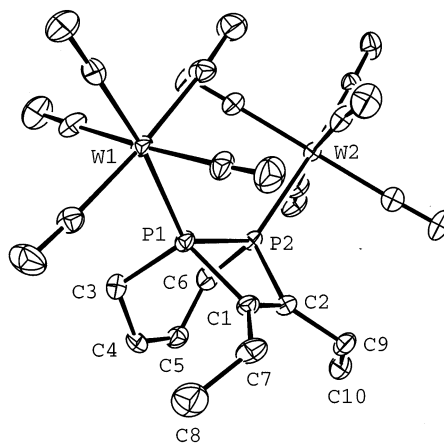
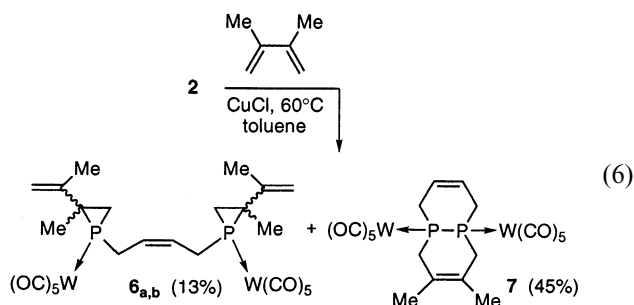
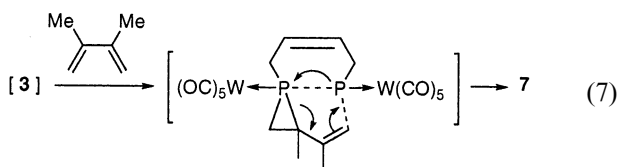


Fig. 1. ORTEP drawing of one molecule of **5**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): W(1)–P(1) 2.497(1), W(2)–P(2) 2.482(1), P(1)–P(2) 2.224(2), P(1)–C(1) 1.845(4), P(1)–C(3) 1.856(6), P(2)–C(2) 1.833(4), P(2)–C(6) 1.838(5), C(1)–C(2) 1.341(7), C(3)–C(4) 1.483(8), C(4)–C(5) 1.308(8), C(5)–C(6) 1.509(7); W(1)–P(1)–P(2) 132.33(6), W(1)–P(1)–C(1) 123.5(2), W(1)–P(1)–C(3) 111.7(2), P(2)–P(1)–C(1) 75.8(2), P(2)–P(1)–C(3) 100.9(2), C(1)–P(1)–C(3) 106.2(2), W(2)–P(2)–P(1) 126.43(6), W(2)–P(2)–C(2) 124.2 (2), W(2)–P(2)–C(6) 114.5(2), P(1)–P(2)–C(2) 76.3(2), P(1)–P(2)–C(6) 101.7(2), C(2)–P(2)–C(6) 106.7(2), P(1)–C(1)–C(2) 103.8(3), P(2)–C(2)–C(1) 103.8(3).

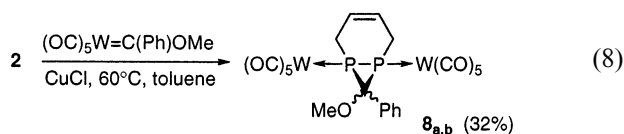


The identity of **6a,b** was easily ascertained. The high-field shift of their ^{31}P resonances at -145.6 and -150.8 (CDCl_3) establishes the presence of the three-membered rings. The mass spectrum indicates that **6a,b** results from the addition of two molecules of 2,3-dimethylbutadiene to one molecule of **3** (m/z 928 for ^{184}W). A close inspection of the ^{31}P resonance of **7** at -43.9 in CDCl_3 shows two ^{31}P – ^{183}W couplings of 162.9 [$^1J(\text{P}–\text{W})$] and 85.7 Hz [$^2J(\text{P}–\text{W})$], respectively, implying the presence of a $\text{W}–\text{P}–\text{P}–\text{W}$ unit. The mass spectrum of **7** displays a molecular peak at m/z 846, indicating that **7** results from the addition of one molecule of diene to one molecule of **3**. The symmetry of the structure is demonstrated by the ^1H and ^{13}C spectra showing one type of CH_3 , two types of CH_2 and one type of vinylic CH resonances. Thus the 1,6-diphosphabicyclo[4.4.0]deca-3,8-diene structure is established beyond any doubt. Once again two mechanisms of formation are possible. The first one would involve a $\text{P}=\text{P}$ coupling followed by a $[4+2]$ cycloaddition between the $\text{P}=\text{P}$ double bond and the diene. A similar cycloaddition involving a diphosphene dicomplex has been described earlier [7]. However the formation of the bis-(vinylphosphirane) complexes **6a,b** leads us to prefer the mechanism depicted in Eq. (7).



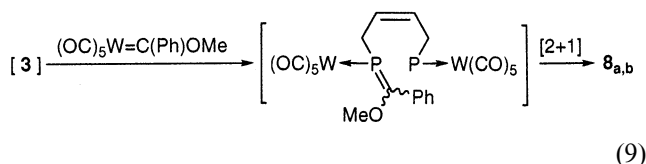
We are currently checking the implications of that hypothesis.

The reaction of **2** with Fischer carbene complexes fits the general pattern presented in our previous mechanistic speculations (Eqs. (5) and (7)). Indeed, the reaction of **2** with (methoxy)(phenyl)carbene-pentacarbonyl-tungsten complex leads to a diphosphirane ring (Eq. (8)).



The product **8a,b** is a mixture of two isomers as shown by its ^{31}P spectrum which displays two resonances at

-93.5 and -101.0 , indicating the presence of a three-membered ring. The mass spectrum shows a molecular peak at m/z 884, demonstrating that **8** results from the addition of one molecule of carbene to one molecule of **3**. The postulated mechanism is depicted in Eq. (9):



The first step mimics the formation of $\text{P}=\text{C}$ double bonds from phosphinidene and carbene complexes [8]. The second step is analogous to the synthesis of diphosphiranes from phosphalkenes and terminal phosphinidene complexes [9].

Thanks to their reactive $\text{P}–\text{P}$ bonds, the three bicyclics **5**, **7** and **8** described in this work are interesting starting points for the synthesis of a variety of new seven-, eight-, and ten-membered diphosphorus rings. Work is in progress to evaluate these possibilities.

3. Experimental

All reactions were performed under nitrogen; the solvents were purified, dried and degassed by standard techniques. ^1H -, ^{13}C -, and ^{31}P -NMR spectra were recorded on a Bruker AC 200 SY spectrometer operating at 200.13, 50.32, and 81.01 MHz, respectively. All chemical shifts are reported in ppm downfield from internal TMS (^1H and ^{13}C) and external 85% H_3PO_4 (^{31}P). Mass spectra (EI) were obtained at 70 eV by the direct inlet method.

3.1. [1,4-Bis-(3,4-dimethylphospholyl)-cis-2-butene]-decarbonylditungsten (**1**)

The [1-lithio-3,4-dimethylphosphole]pentacarbonyl-tungsten complex was prepared as described in a previous publication [10]. The resulting solution in THF was allowed to react with a half equivalent of 1,4-dichloro-*cis*-2-butene between -40°C and room temperature. The bis-phospholyl complex **1** was isolated by chromatography on silica gel with hexane/dichloromethane 4:1 as the eluent. A yellow powder was thus obtained in 25% yield (not optimized). ^{31}P -NMR (CDCl_3): δ 4.5, $^1J(^{31}\text{P}–^{183}\text{W}) = 204.7$ Hz. ^1H -NMR (CDCl_3): δ 2.16 (s, 12H, Me), 2.70 (m, 4H, CH_2), 5.35 (m, 2H, $\text{CH}=\text{CH}$), 6.24 (d, $^2J(\text{H}–\text{P}) = 36.9$ Hz, 4H, $=\text{CH}–\text{P}$). ^{13}C -NMR (CDCl_3): δ 17.34 (d, $^3J(\text{C}–\text{P}) = 10.6$ Hz, Me), 29.61 (d, $^1J(\text{C}–\text{P}) = 20.9$ Hz, CH_2), 125.32 (s, $\text{CH}=\text{CH}$), 128.50 (d, $^1J(\text{C}–\text{P}) = 41.9$ Hz, $\text{P}–\text{CH} =$), 151.80 (d, $^2J(\text{C}–\text{P}) = 7.2$ Hz, Me–C), 196.21 (*cis* CO); Mass spectrum (^{184}W): m/z 924 (M^+ , 7%), 379 (100%).

3.2. [1,4-Bis-(2,3-bis-methoxycarbonyl-5,6-dimethyl-7-phosphanorbornadien-7-yl)-cis-2-butene]-decacarbonylditungsten (**2**)

A solution of **1** (9.3 g, 1×10^{-2} mol) and dimethyl acetylenedicarboxylate (8 ml) in 30 ml of toluene was heated at 70°C for 48 h. The product was purified by chromatography on silica gel with dichloromethane as the eluent. Yield 50%. ^{31}P -NMR (CDCl_3): δ 207.1, $^1\text{J}(^{31}\text{P}-^{183}\text{W}) = 239.7$ Hz. ^1H -NMR (CDCl_3): δ 1.93 (s, 12H, Me), 3.14 (s, br, 4H, CH_2), 3.59 (d, $^2\text{J}(\text{H}-\text{P}) = 2.2$ Hz, 4H, $\text{P}-\text{CH}$), 3.78 (s, 12H, OCH_3), 5.44 (m, 2H, $\text{CH}=\text{CH}$). ^{13}C -NMR (CDCl_3): δ 16.20 (s, Me), 36.03 (s, $\text{P}-\text{CH}_2$), 52.79 (s, OMe), 59.44 (d, $^1\text{J}(\text{C}-\text{P}) = 19.6$ Hz, $\text{P}-\text{CH}$), 125.28 (d, $^2\text{J}(\text{C}-\text{P}) = 9.3$ Hz, $\text{CH}=\text{CH}$), 139.01 (d, $^2\text{J}(\text{C}-\text{P}) = 16.8$ Hz, $\text{Me}-\text{C}$), 145.57 (s, $\text{C}-\text{CO}_2\text{Me}$), 165.11 (s, CO_2Me), 196.15 (d, $^2\text{J}(\text{C}-\text{P}) = 6.0$ Hz, *cis*-CO), 197.66 (d, $^2\text{J}(\text{C}-\text{P}) = 27.3$ Hz, *trans*-CO). Anal. Calc. for $\text{C}_{38}\text{H}_{34}\text{O}_{18}\text{P}_2\text{W}_2$: C, 37.75; H, 2.81. Found: C, 37.58; H, 2.71.

3.3. [1,4-Bis-(2,3-diethylphosphiren-1-yl)-cis-2-butene]-decacarbonylditungsten (**4**)

A solution of **2** (0.6 g, 5×10^{-4} mol), 3-hexyne (0.35 ml, 3×10^{-3} mol), CuCl (60 mg) in 10 ml of toluene was heated at 60°C for 2.5 h. The product was chromatographed on silica gel with hexane/dichloromethane 5/1 as the eluent. The bis-phosphirene **4** was isolated as a white powder (0.15 g, 30%). ^{31}P -NMR (CDCl_3): δ -158. ^1H -NMR (CDCl_3): δ 1.27 (t, 12H, Me), 2.40 (m, 4H, CH_2), 2.65 (q, CH_2 (Et)), 5.25 (m, 2H, $\text{CH}=\text{CH}$); ^{13}C -NMR (CDCl_3): δ 12.51 (s, Me), 20.50 (d, CH_2-Me), 38.06 (d, $^1\text{J}(\text{C}-\text{P}) = 5.2$ Hz, $\text{P}-\text{CH}_2$), 125.61 (s, $\text{CH}=\text{CH}$), 133.53 (d, $^1\text{J}(\text{C}-\text{P}) = 14.8$ Hz, $\text{P}-\text{C}$ (Et)), 196.73 (d, $^2\text{J}(\text{C}-\text{P}) = 7.6$ Hz, *cis* CO). MS (^{184}W): m/z 928 (M^+ , 8.6%), 437 (100%).

3.4. [7,8-Diethyl-1,6-diphosphabicyclo[4.2.0]octa-3,7-diene]decacarbonylditungsten (**5**)

A solution of **2** (0.42 g, 3.5×10^{-4} mol), 3-hexyne (0.12 ml, 1×10^{-3} mol), CuCl (40 mg) in 10 ml of toluene was heated at 60°C for 3 h. According to the ^{31}P spectrum of the reaction mixture, **4** and **5** were formed in a 1:2 ratio. The products were separated by chromatography on silica gel with hexane/dichloromethane 10/1 as the eluent. The bicycle **5** was isolated as a white powder (0.12 g, 40%). ^{31}P -NMR (CDCl_3): δ 7.5. ^1H -NMR (CDCl_3): δ 1.06 (t, 6H, CH_3), 2.39 (m, 4H, CH_2Me), 2.68 and 3.07 (2 m, 4H, CH_2P), 5.89 (m, 2H, $\text{CH}=\text{CH}$). ^{13}C -NMR (CDCl_3): δ 13.49 (s, Me), 24.19 (pseudo t, CH_2Me), 35.14 (s, CH_2P), 125.87 (s, $\text{CH}=\text{CH}$), 153.73 (pseudo t, $\text{P}-\text{C}-\text{Et}$). MS (^{184}W): m/z 846 (M^+ , 26%), 564 ($M^+ - 10 \text{ CO}$, 100%). Anal.

Calc. for $\text{C}_{20}\text{H}_{16}\text{O}_{10}\text{P}_2\text{W}_2$: C, 28.36; H, 1.89. Found: C, 27.81; H, 2.02.

3.5. [1,4-Bis-(2-methyl-2-propenylphosphiran-1-yl)-cis-2-butene]decacarbonylditungsten (**6a,b**) and [3,4-Dimethyl-1,6-diphosphabicyclo[4.4.0]deca-3,8-diene]decacarbonylditungsten (**7**)

A solution of **2** (0.5 g, ca. 0.4×10^{-3} mol), 2,3-dimethyl-1,3-butadiene (0.1 ml, ca. 0.8×10^{-3} mol), CuCl (60 mg) in toluene (7 ml) was heated at 60°C for 2 h. The products were separated by chromatography on silica gel with hexane as the eluent. The first fraction contained a mixture of **6a,b** (50 mg, 13%); the second fraction contained **7** (160 mg, 45%). **6a,b** ^{31}P -NMR (CDCl_3): δ -145.57 and -150.86 (1:1). MS (^{184}W): m/z 928 (M^+ , 6%), 379 (100%). **7** ^{31}P -NMR (CDCl_3): δ -43.94, $^1\text{J}(^{31}\text{P}-^{183}\text{W}) = 162.9$, $^2\text{J}(^{31}\text{P}-^{183}\text{W}) = 85.7$ Hz. ^1H -NMR (CDCl_3): δ 1.83 (s, 6H, Me), 2.73 and 2.95 (2 m, 8H, CH_2), 5.88 (m, 2H, $\text{CH}=\text{CH}$). ^{13}C -NMR (CDCl_3): δ 22.89 (pseudo t, Me), 27.93 (pseudo t, CH_2P), 35.38 (pseudo t, CH_2P), 124.17 and 124.22 (2 s, CH and C sp^2 ; assignments checked by parity experiments), 196.27 (*cis* CO). MS (^{184}W): m/z 846 (M^+ , 22%), 650 (100%).

3.6. [7-Methoxy-7-phenyl-1,6-diphosphabicyclo[4.1.0]hept-3-ene]decacarbonylditungsten (**8a,b**)

A solution of **2** (0.85 g, 7×10^{-4} mol), carbene complex (1.7 g, 3.8×10^{-3} mol), CuCl (100 mg) in 20 ml of toluene was heated at 60°C for 3 h. The product was purified by chromatography on silica gel with hexane as the eluent. ^{31}P -NMR (CDCl_3): δ -101.0 and -93.5. ^1H -NMR (CDCl_3): δ 3.26 and 3.33 (2 s, OMe), 5.61 and 6.34 (2 m, $\text{CH}=\text{CH}$). ^{13}C -NMR (CDCl_3): δ 29.05 and 31.26 (2 s, CH_2P), 55.43 and 58.19 (2 t, $^3\text{J}(\text{C}-\text{P}) = 7.5$ and 4.5 Hz, OMe), 79.50 and 80.50 (2 t, $^1\text{J}(\text{C}-\text{P}) = 7.8$ and 16.8 Hz, $\text{C}-\text{OMe}$), 126.44 (s, $\text{CH}=\text{CH}$). MS (^{184}W): m/z 884 (M^+ , 26%), 662 (100%). Anal. Calc. for $\text{C}_{22}\text{H}_{14}\text{O}_{11}\text{P}_2\text{W}_2$: C, 29.86; H, 1.58. Found: C, 29.36; H, 1.86.

4. X-ray structure determination for **5**

A crystal of **5** ($\text{C}_{20}\text{H}_{16}\text{O}_{10}\text{P}_2\text{W}_2$, colorless cube 0.32 $\times$ 0.32 $\times$ 0.32 mm) was grown from a dichloromethane-pentane solution of the compound. Data were collected at 123 ± 0.5 K on an Enraf-Nonius CAD4 diffractometer using Mo- K_α ($\lambda \pm 0.71073$ Å) radiation and a graphite monochromator. Psi scan absorption corrections ($T_{\min} = 0.59$, $T_{\max} = 1.00$) were applied. The crystal structure was solved and refined using the Enraf-Nonius MOLEN package. The compound crystallises in space group $P\bar{1}$ ($\neq 2$), $a = 7.397(1)$ Å, $b =$

9.254(1) Å, $c = 18.822(2)$ Å, $\alpha = 94.58(1)^\circ$, $\beta = 94.45(1)^\circ$, $\gamma = 105.78(1)^\circ$; $V = 1229.30(54)$ Å³; $Z = 2$; $D_{\text{calc.}} = 2.285$ g cm⁻³; $\mu = 97.3$ cm⁻¹; $F(000) = 788$. A total of 6408 unique reflexions were recorded in the range $2^\circ \leq \theta \leq 56.1^\circ$ of which 1246 were considered as unobserved ($F^2 < 3.0\sigma(F^2)$), leaving 5162 for solution and refinement. Direct methods yielded a solution for all atoms. The hydrogen atoms were included as fixed contributions in the final stages of least-squares refinement while using anisotropic temperature factors for all other atoms. A non-Poisson weighting scheme was applied with a p factor equal to 0.08. The final agreement factors were $R = 0.027$, $R_w = 0.049$, goodness-of-fit = 1.28.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 103100 for **6**. Copies of the information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: de-

posit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>.

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