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Preliminary communication

Different reaction modes of supermesitylphosphaalkyne with $[W(CO)_5thf]$-unusual C-H-activation forming an indanyl substituent [1]

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Abstract

Treatment of the phosphaalkyne $P{\equiv}CAr'$ **1** with $[W(CO)_5(thf)]$ leads to the complex $[W(CO)_2\{\eta^2\text{-}PCAr')W(CO)_5\}_2]$ **2** ($Ar' = C_6H_2^tBu_3$-2,4,6) with two side-on coordinated phosphaalkyne moieties. In the presence of equimolar amounts of $[W_2(O^tBu)_6]$, however, the formation of $[W(CO)_4P(R')C(Ar')P\{W(CO)_5\}]$ **3** ($R' = 2,4\text{-}^tBu_2\text{-}7\text{-}Me_2$-indanyl) is observed. **3** is a product of a 'head-to-tail' dimerisation of the former phosphaalkynes **1** to give a novel phosphinidene complex containing an indanyl substituent formed via C–H-activation. © 1998 Elsevier Science S.A.

Keywords: Supermesitylphosphaalkyne; Tungsten complexes; Dimerisation; Phosphinidene complexes; C–H-Activation

1. Introduction

The coordination chemistry of $^tBuC{\equiv}P$ has been extensively investigated [1–3]. Examples for the use of sterically more bulky derivatives such as the supermesityl substituted phosphaalkyne **1** are very rare [4]. Recently, Jones et al. [5] reported the reaction between $Ar'C{\equiv}As$ ($Ar' = C_6H_2^tBu_3$-2,4,6) and $[W(CO)_5thf]$, which resulted in the formation of the 1,3-diarsacyclobutadiene **4** and the 1,2-diarsetane complex **5**. Our approach in this field is focused on the use of phosphaalkynes in the metathesis reaction with $[W_2(O^tBu)_6]$ in the presence of $[M(CO)_5thf]$ (M = Cr, W) in order to generate complexes with tungsten phosphorus triple bond of the type $[(^tBuO)_3W{\equiv}P \rightarrow M(CO)_5]$ **6** [6] and the alkylidyne complex $[(^tBuO)_3W{\equiv}CR]$. A subsequent reaction with additional $^tBuC{\equiv}P$, however, followed by 1,3-migration of the alkoxy ligand to form compounds with four-membered rings, cannot entirely be prevented. Due to the considerable sensitivity of the alkoxide products the reaction mixture could not be separated by column chromatography. Enrichment of **6** in solution could only be achieved by fractional crystallization. Recently, Cummins et al. [7,8] and Schrock et al. [9,10] succeeded in the synthesis of the first isolated and structurally characterised complexes with terminal phosphido ligands **7** and **8**. In both molecular structures the metal–phosphorus triple bond is protected by bulky amide ligands. Our investigations revealed that **8** reacts predominantly to give end-on coordination, which is due to reactions of the lone pair of the phosphido phosphorus rather than the metal–phosphorus triple

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[1] Dedicated to Professor A. Zschunke on the occasion of his 60th birthday.

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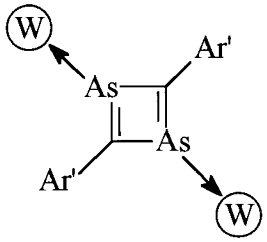
bond [11,12]. Our interest, however, is mainly focused on the side-on reactivity of these compounds as found for complexes such as **6**.



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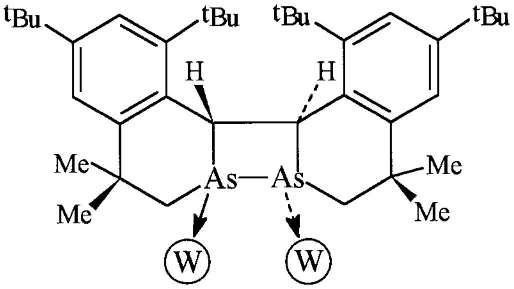

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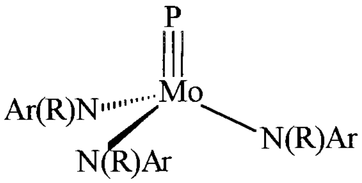
Ar' = $C_6H_2{}^tBu_3$-2,4,6

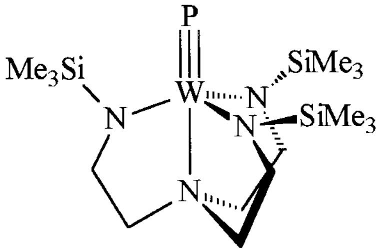
Ⓦ = $W(CO)_5$



Ar = 3,5-$(CH_3)_2C_6H_2$

R = $C(CD_3)_2CH_3$

7



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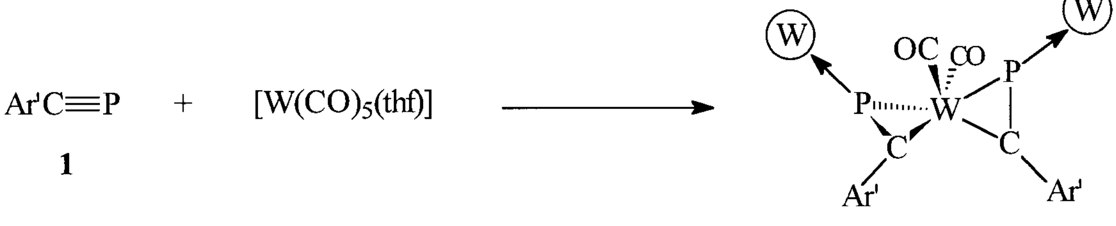
In order to prevent cyclisation products of **6** with $^tBuC{\equiv}P$, we increased the sterical demand of the phosphaalkyne, employing the bulky supermesityl rest Ar′. However, before one can study the conversion of $[W_2(O^tBu)_6]$ with **1** in the presence of $[W(CO)_5(thf)]$, it is essential to establish the reaction behaviour of Ar′C≡P with $[W(CO)_5(thf)]$ only. Interestingly, Ar′C≡P **1** displays entirely different reactivity in comparison to $^tBuC{\equiv}P$ [6], which we report herein.

2. Results and discussion

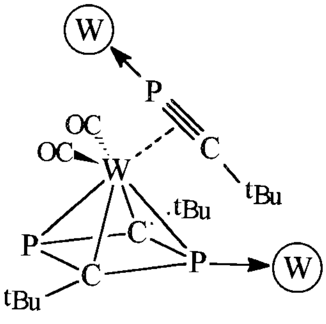
The reaction of **1** with equimolar amounts of $[W(CO)_5(thf)]$ at ambient temperature resulted in the low-yield formation of the spirocyclic complex $[W(CO)_2\{(\eta^2\text{-PCAr}')W(CO)_5\}_2]$ **2** (Eq. (1)) which was purified by column chromatography. The low yield was mainly due to the majority of Ar′C≡P being unreacted and obtained back after the chromatographic work up. Even employment of more vigorous reaction conditions could not increase the yield. The red crystalline complex **2** is readily soluble in all common organic solvents and air stable for short periods. Interestingly, there is no cyclodimerisation as found in the corresponding reaction with $^tBuC{\equiv}P$ to give the 1,3-diphosphacyclobutadiene complex **9** [6].



1 (1)

Ar' = $C_6H_2{}^tBu_3$-2,4,6

2



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Ⓦ = W(CO)$_5$

The $^{31}P\{^1H\}$ NMR spectrum of **2** reveals a singlet at 318.2 ppm bearing two pairs of tungsten satellites with coupling constants $^1J_{WP}$ of 254.2 Hz and 24.6 Hz, respectively. The first coupling constant is consistent for a phosphorus atom coordinating to a W(CO)$_5$-moiety; the latter indicates the side-on coordination to a tungsten carbonyl fragment. $^1J_{WP}$ coupling constants of side-on coordinated phosphaalkynes are small due to the low s-character of this bond [13].

The dominant feature of the molecular structure of **2** (Fig. 1) is a central W(CO)$_2$ unit. Two phosphaalkyne moieties bind side-on in η^2-manner to this tungsten atom. The P atoms further coordinate to W(CO)$_5$-groups. The bonding distance between C(7) and P(1) at 1.677(11)Å is consistent with an average P–C-double bond as found in phosphaalkenes of the type $R_2C=PR'$ (1.67 Å) [14]. Both W–P–C triangular planes are twisted 70.98(32)° to each other. The Ar′ moieties are disordered.

The difference in reactivity of **1** in comparison to ^{t}BuC≡P is due to the increased bulk of the supermesityl rest of the phosphaalkyne. This leads to the assumption that in the first step of the reaction the phosphaalkyne coordinates end-on to a W(CO)$_5$-group. This activated molecule reacts—depending on the residue R—with another equivalent of phosphaalkyne under loss of CO to form either a cyclo-C_2P_2 ring or compound **2**. Due to the great sterical demand of the supermesityl rest the approach of another molecule of **1** in order to form a Ar′C)$_2$P$_2$ ring is impossible.

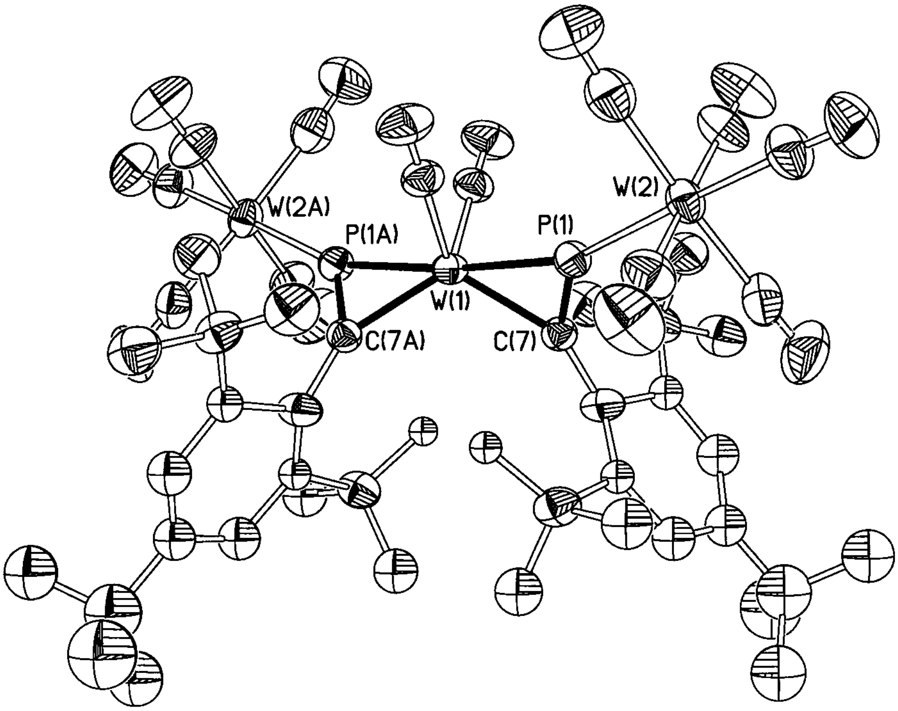
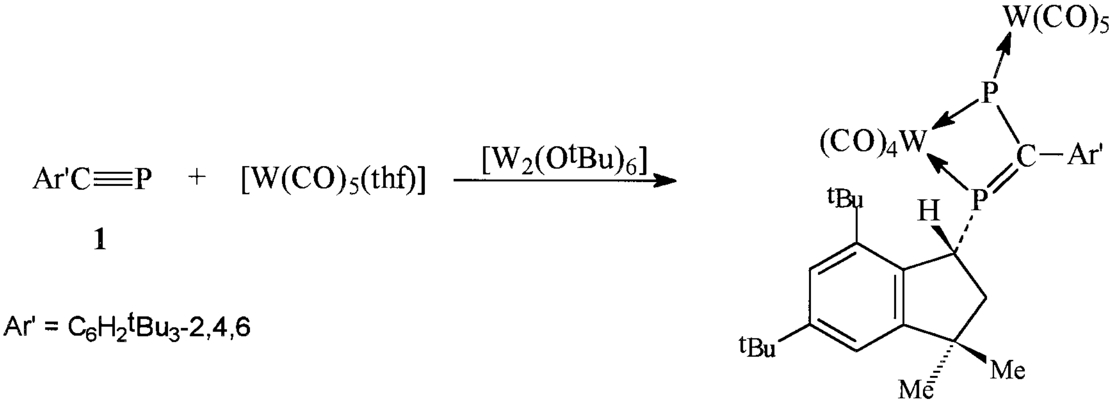


Fig. 1. Molecular structure of **2** (only one position of the Ar′ rings is drawn for clarity). Selected bond lengths (Å) and angles (°): P–C(7) 1.677(11), P–W(1) 2.412(3), P–W(2) 2,438(3), C(7)–W(1) 2.069(10), P–C(7)–W(1) 79.4(4), C(7)–W(1)–P 43.1(3), W(1)–P–C(7) 140.6(4).

Knowing about the reaction behaviour of **1** with [W(CO)$_5$(thf)] we were able to start our investigation concerning the conversion of [W$_2$(O^{t}Bu)$_6$] with **1** in the presence of [W(CO)$_5$(thf)] at −21°C. The ^{31}P{^{1}H} NMR spectra of the crude reaction mixture indicated the formation of **2** and **3** in about equal amounts besides relatively large quantities of unreacted **1**. The yield of **3** could be increased when the reaction was performed at ambient temperature.



3

3 crystallises in the form of dark green plates and is soluble in all common organic solvents including pentane. In the solid state **3** is air stable for short periods. In solution the compound appears to be more sensitive. The ^{31}P{^{1}H} NMR spectrum of **3** indicates the existence of two chemically different phosphorus atoms. One signal exhibits a strong shift towards downfield at 787.3 ppm. This is in range for phosphinidene P atoms. Additionally, the satellite pattern implies the coordination to two tungsten carbonyl fragments with $^1J_{WP}$ 186 Hz and 117 Hz, respectively. This is in good correspondence with data found for other tungsten phosphinidene complexes (e.g., [Cp*P{W(CO)$_5$}$_2$] 1076.2 ppm, $^1J_{WP}$ 187.6 Hz, 165.7 Hz [M. Scheer, E. Leiner, unpublished results]; [2-^{i}Pr-5-MeC$_6$H$_{10}$P{W(CO)$_5$}$_2$]

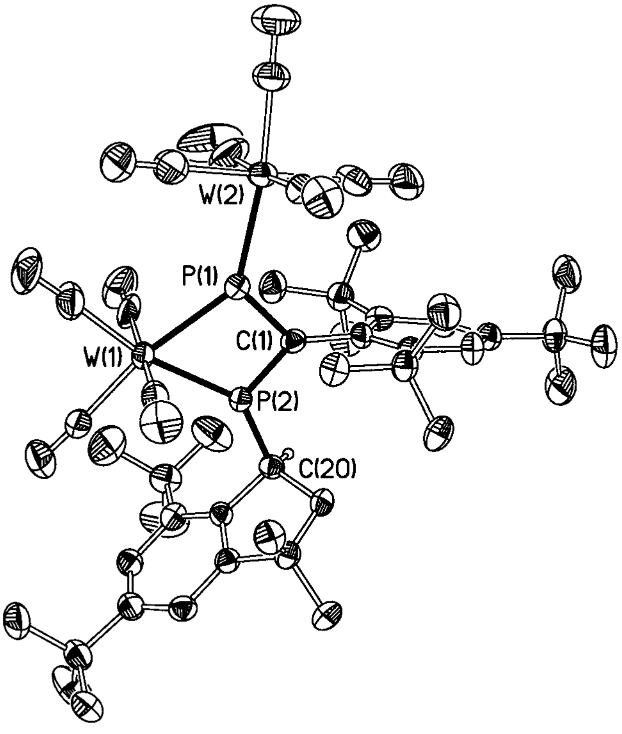


Fig. 2. Molecular structure of **3**: Selected bond lengths (Å) and angles (°): P(1)–W(1) 2.464(2), P(1)–W(2) 2.443(2), P(1)–C(1) 1.803(6), P(2)–W(1) 2.411(2), P(2)–C(1) 1.716(6), P(2)–C(20) 1.860(6), P(1)–C(1)–P(2) 96.1(3), W(1)–P(1)–C(1) 97.2(2), W(1)–P(2)–C(1) 101.7(2), P(1)–W(1)–P(2) 64.9(3).

1041 ppm, $^1J_{WP}$ 168 Hz [15]). The second signal is observed at 313.9 ppm revealing only one pair of satellites ($^1J_{WP} = 202$ Hz).

The molecular structure of **3** (Fig. 2) reveals a ‘head-to-tail’ dimer of two phosphaalkyne molecules forming a phosphinidene ligand. The phosphinidene phosphorus P(1) is bonded to the C(1) atom via a single bond [1.806(3) Å]. Both phosphorus atoms P(1) and P(2) further coordinate to a $W(CO)_4$-moiety creating a planar and slightly distorted four-membered ring. The bonding distance between P(2) and C(1) corresponds to a double bond [14] P(1) additionally binds to a $W(CO)_5$-fragment. The bonding distances P(1)–W(1) (2.412(2) Å) and P(1)–W(2) (2.443(2) Å) are in the range for phosphinidene complexes (e.g., $Cp^*P[W(CO)_5]_2$), W–P-distance 2.445(2) Å, 2.428(2) Å) [M. Scheer, E. Leiner, unpublished results] [16].

Obviously, the influence of $[W_2(O^tBu)_6]$ is responsible for the ‘head-to-tail’ dimerisation of **1**, yielding the novel phosphinidene complex $[W(CO)_4P(R')C\ (Ar')P\{W(CO)_5\}]$ **3** (R′ = 2,4-^{t}Bu$_2$-7-Me$_2$-indanyl). The function of $[W_2(O^tBu)_6]$, however, is uncertain. Experiments showed, that stoichiometric amounts of $[W_2(O^tBu)_6]$, $[W(CO)_5(thf)]$ and **1** are essential for the formation of **3**. After the ‘head-to-tail’ dimerisation the C(20)-atom becomes unsaturated. Subsequently, a C–H-activation involving a 1,2-H-shift from the methyl group of one of the *ortho*-tertiary butyl groups to C(20) occurs and leads to a five-membered ring. C–H-activations are common for systems containing supermesityl groups ($C_6H_2^tBu_3$-2,4,6) and a hetero atom at position 1 of the aromatic ring [17–19]. Usually, five-membered rings containing a heteroatom (e.g., P [17,18] or Ge [19]) are generated. To the best of our knowledge this is the first example for the creation of a five-membered indanyl ring system with ring closure to a carbon atom. Recently, Jones et al. [5] showed the formation of a six-membered ring as in complex **5**.

3. Experimental

All experiments were performed under argon in anhydrous solvents using standard Schlenk or glove box techniques. ^{1}H NMR and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AC 250 spectrometer in C_6D_6 at 25°C (^{1}H: 250.13 MHz; ^{31}P: 101.256 MHz; standard: TMS (^{1}H), 85% H_3PO_4(^{31}P)). Mass spectra were obtained on a Finnigan MAT 311 ADF spectrometer at 70 eV. The IR spectra were recorded on a Perkin-Elmer PE 883.

3.1. Starting materials

1 was prepared according to a modified procedure as described in Ref. [20]. $[W_2(O^tBu]_6]$ was synthesized according to Ref. [21]

3.2. $[W(CO)_2\{(\eta^2\text{-}PCAr')W(CO)_5\}_2]$ **2** ($Ar' = C_6H_2^tBu_3$-2,4,6)

To a solution of $[W(CO)_5(thf)]$ (1.29 mmol) in THF (25 ml) **1** (372 mg, 1.29 mmol) was added. The mixture was stirred for three days at room temperature. Then the solvent was removed in vacuo. Subsequently, $W(CO)_6$ was removed by sublimation. The crude product was purified by column chromatography using silicagel and hexane. The first fraction was eluted with hexane and afforded only unreacted $Ar'C{\equiv}P$ **1**. **2** could be isolated from the second fraction as a red crystalline compound and was recrystallised from hexane. Isolated yield: 113 mg (6%). $^{31}P\{^1H\}$ NMR (101 MHz, C_6D_6, 298 K) δ 318.2 ppm, $^1J_{WP}$ 254.2 Hz, 24.6 Hz; ^{1}H NMR (250 MHz, C_6D_6, 298 K) δ 1.21 ppm (s, 18H), δ 1.28 ppm (s, 9H), δ 7.52 ppm (s, 2H) $\upsilon(CO)/cm^{-1}$ 2085s, 2077vs, 2015s, 2007s, 1985vs, 1951vs, br.

3.3. $[W(CO)_4P(R')C(Ar')P\{W(CO)_5\}]$ **3** (R′ = 2,4-^{t}Bu$_2$-7-Me$_2$-indanyl)

To a mixture of $[W_2(O^tBu)_6]$ (569 mg, 0.72 mmol) and $[W(CO)_5(thf)]$ (0.72 mmol) in THF (30 ml) **1** (200 mg, 0.72 mmol), dissolved in hexane (40 ml), was added dropwise over a period of one hour at room temperature. The solution was stirred for an additional hour. Then the solvent was removed in vacuo and $W(CO)_6$ was removed by sublimation. **3** was recrystallised from pentane in the form of dark green plates at 0°C. Isolated yield: 172 mg (20%). $^{31}P\{^1H\}$ NMR (101 MHz, C_6D_6, 298 K) δ 787.3 ppm, $^1J_{WP}$ 186 Hz, 117 Hz; δ 313.9 ppm, $^1J_{WP}$ 202 Hz; ^{1}H NMR (250 MHz, C_6D_6, 298 K) δ 1.26 (s, 9H, ^{t}Bu), δ 1.29 ppm (s, 9H, ^{t}Bu), δ 1.41 ppm (s, 9H, ^{t}Bu), δ 1.49 ppm (s, 6H), δ 1.79 ppm (s, 9H, ^{t}Bu), δ 1.84 ppm (s, 9H, ^{t}Bu), δ 7.39 ppm (d, 2H), δ 7.715 ppm (d, 2H). $\upsilon(CO)/cm^{-1}$ 2078s, 2064w, 2017s, 2003w, 1965vs, br, 1941 vs, sh, 1915s. EI-MS (70 eV, 100°C): m/z 1197.2 (M^+, 1), 882.5 ($M'-W(CO)_5$, 8), 351.7 ($W(CO)_6^+$, 24), 288 ($Ar'{\equiv}CP^+$, 58), 257 ($Ar'{\equiv}C$, 100). Anal. Calcd for $W_2P_2O_9C_{47}H_{58}$: C, 47.17; H, 4.85. Found: C, 47.21, H 4.81.

*3.4. X-ray crystallography of **2** and **3***

Crystal structure analyses were performed on STOE IPDS **2** and STOE STADI IV **3**: ω-scan mode) diffractometers with Mo-K_α radiation ($\lambda = 0.71073$ Å) with emperical absorption corrections for **3** (5 Psi-scans): **2**: $C_{50}H_{58}O_{12}P_2W_3$, $M = 1464.45$, monoclinic, space group $C2/c$ (No. 15), $a = 20.212(4)$, $b = 22.533(5)$, $c = 12.908(3)$Å, $\beta = 104.99(3)°$, $U = 5679(2)$ Å^3, $Z = 4$, $d_c = 1.713$ Mg m^{-3}, $F(000) = 2824$, $\mu = 61.72$ cm^{-1}, 273 parameters, crystal size $0.33 \times 0.19 \times 0.08$ mm, $T = 200(1)$ K, $3.6 < 2\theta < 52.3°$. Number of reflections measured 15701, 5615 independent reflections [R(int) = 0.0361] of which 4225 were assigned observed [$I > 2\sigma(I)$], absorption coefficient 6.172 mm^{-1}. The refinement converged at residuals $wR_2 = 0.0772$ for all reflections, corresponding to a conventional $R = 0.0287$ for the observed F_0 data. **3**: $C_{47}H_{58}O_9P_2W_2$, $M = 1196.57$, triclinic, space group $P\bar{1}$, $a = 10.629(4)$, $b = 12.697(5)$, $c = 19.433(7)$ Å, $\alpha = 106.41(3)°$, $\beta = 99.37(3)°$, $\gamma = 91.27(3)°$, $U = 2476(2)$ Å^3, $Z = 2$, $d_c = 1.605$ Mg m^{-3}, $F(000) = 1180$ $\mu = 45.75$ cm^{-1}, 558 parameters, crystal size $0.38 \times 0.30 \times 0.08$ mm, $T = 200(1)$ K $3.2 < 2\theta < 52°$. Number of reflections measured 9002, 9002 independent reflections [R(int) = 0.000] of which 6580 were assigned observed [$I > 2\sigma(I)$], absorption coefficient 4.575 mm^{-1}. The refinement converged at residuals $wR_2 = 0.1127$ for all reflections, corresponding to a conventional $R = 0.0396$ for the observed F_0 data. Both structures were solved by direct methods using SHELXS-86 [22], full-matrix-least-squares refinement on F^2 in SHELXL-93 [23] with anisotropic displacement for non-H atoms, hydrogen atoms located in idealized positions and refined isotropically according to the riding model.

Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH; D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository numbers CSD-407514 and CSD-407515, the names of the authors and the journal citation.

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References

[1] P. Binger, Multiple Bonds and Low Coordination in Phosphorus Chemistry, in: M. Regitz, O.J. Scherer (Eds.), Thieme, Stuttgart, 1990, p. 90.
[2] J.F. Nixon, Chem. Rev. 88 (1988) 1327.
[3] J.F. Nixon, Coord. Chem. Rev. 145 (1995) 201–258.
[4] M. Scheer, A. Krug, P. Kramkowski, J.F. Corrigan, Organometallics, accepted.
[5] M.D. Francis, D.E. Hibbs, M.B. Hursthouse, C. Jones, K.M.A. Malik, J. Chem. Soc., Chem. Commun., 1996, p. 631.
[6] M. Scheer, K. Schuster, T.A. Budzichowski, M.H. Chisholm, W.E. Streib, J. Chem. Soc., Chem. Commun., 1995, p. 1671.
[7] C.E. Laplaza, W.M. Davis, C.C. Cummins, Angew. Chem. 107 (1995) 2181.
[8] C.E. Laplaza, W.M. Davis, C.C. Cummins, Angew. Chem. Int. Ed. Engl. 34 (1995) 2042.
[9] N.C. Zanetti, R.R. Schrock, W.M. Davis, Angew. Chem. 107 (1995) 2184.
[10] N.C. Zanetti, R.R. Schrock, W.M. Davis, Angew. Chem. Int. Ed. Engl. 34 (1995) 2044.
[11] M. Scheer, J. Müller, M. Häser, Angew. Chem. 108 (1996) 2637–2641.
[12] M. Scheer, J. Müller, M. Häser, Angew. Chem. Int. Ed. Engl. 35 (1996) 2492–2496.
[13] J.C.T.R. Burckett-St. Laurent, P.B. Hitchcock, H.W. Kroto, J.F. Nixon, J. Chem. Soc., Chem. Commun., 1981, p. 1141.
[14] R. Appel, Multiple Bonds and Low Coordination in Phosphorus Chemistry, in: M. Regitz, O.J. Scherer (Eds.), Thieme, Stuttgart, 1990 p. 160.
[15] A.M. Hinke, M. Hinke, W. Kuchen, Z. Naturforsch., Teil B 41 (1986) 629.
[16] G. Huttner, L. Lang, Multiple Bonds and Low Coordination in Phosphorus Chemistry, in: M. Regitz, O.J. Scherer (Eds.), Thieme, Stuttgart, (1990) p. 48.
[17] M. Yoshifuji, T. Sato, N. Inamoto, Chem. Lett., 1988 p. 1735.
[18] D.H. Champion, A.H. Cowley, Polyhedron 4 (1985) 1791.
[19] L. Lange, B. Meyer, W.-W. du Mont, J. Organomet. Chem. 329 (1987) C17–C20.
[20] J. Sejpka, PhD thesis, Univ. of Regensburg, 1987.
[21] M.H. Chisholm, B.W. Eichhorn, K. Folting, J.C. Huffmann, C.D. Ontiveros, W.E. Streib, W.G. Van Der Sluys, J. Am. Chem Soc. 26 (1987) 3182.
[22] G.M. Sheldrick, SHELXS-86, Univ. of Göttingen, 1986.
[23] G.M. Sheldrick, SHELXL-93, Univ. of Göttingen, 1993.