


Short Note

# (Decacarbonyl)(1-isopropyl-2-phenyl-1,2,5,6-tetrahydroacenaphtho [5,6-cd][1,2]diphosphole)ditungsten(0)

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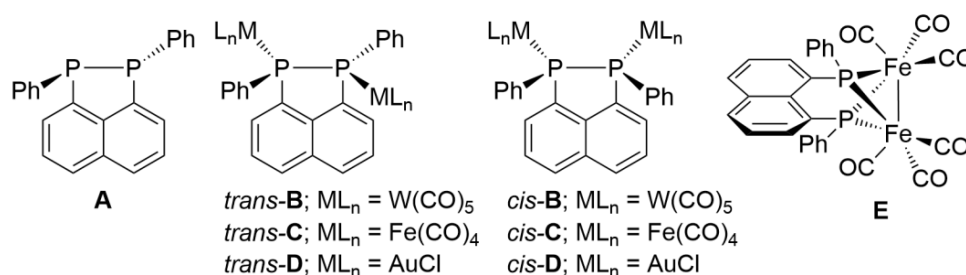
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**Abstract:** A binuclear tungsten(0) complex with an asymmetric bridging 1,2-diphosphole ligand was prepared by the photolysis of tungsten hexacarbonyl in the presence of 1-isopropyl-2-phenyl-1,2,5,6-tetrahydroacenaphtho [5,6-cd][1,2]diphosphole. The tungsten complex **1** was characterized by high resolution mass spectrometry, multinuclear NMR spectroscopy ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$ ), and elemental microanalysis. The structure of the *trans* isomer was resolved by single crystal X-ray diffraction, showing a slight elongation of the P–P bond upon coordination to the  $\text{W}(\text{CO})_5$  groups.

**Keywords:** X-ray crystallography; NMR spectroscopy; inert atmosphere synthesis; phosphorus; tungsten; binuclear complex

## 1. Introduction

The symmetrically functionalised, 1,2-diphenyl-1,2-dihydronaphtho[1,8-cd][1,2]diphosphole (**A**) (Figure 1) has been shown to react with metals forming binuclear species, where the metal groups can be *cis* and *trans* to one another, with the P–P bond remaining intact [1,2]. Although the heating of **A** with  $\text{W}(\text{CO})_6$  under UV irradiation results in a mixture of the *cis* and *trans* isomers (**B**), the *cis*-**B** isomer was prepared exclusively by separate stepwise reactions [3]. The *cis* isomers are reported to be much less thermodynamically stable than the *trans* isomers due to an increased steric repulsion between the two metal centres [3]. This is seen in *cis*-**B** and *trans*-**B**, where the P–P bond length is marginally longer in the *cis* isomer (2.280(2) vs. 2.270(1) Å, respectively).



**Figure 1.** Structures of rigid naphthalene-based 1,2-diphospholes.

Using the symmetrically rigid 1,2-diphosphole **A**, Mizuta *et al.* produced a series of complexes bearing various transition metals such as Fe, Au, and W [1–3]. With the metal carbonyl complexes **B** and **C**, the *trans* isomer was the most stable. Upon stirring at ambient conditions for several days, *cis*-**C** converted to **E** with the loss of CO, the formation of an Fe–Fe bond, and the breaking of the P–P bond (P···P separation in **E** is 2.7377(6) Å). No such reactions were observed for the *trans* isomers.



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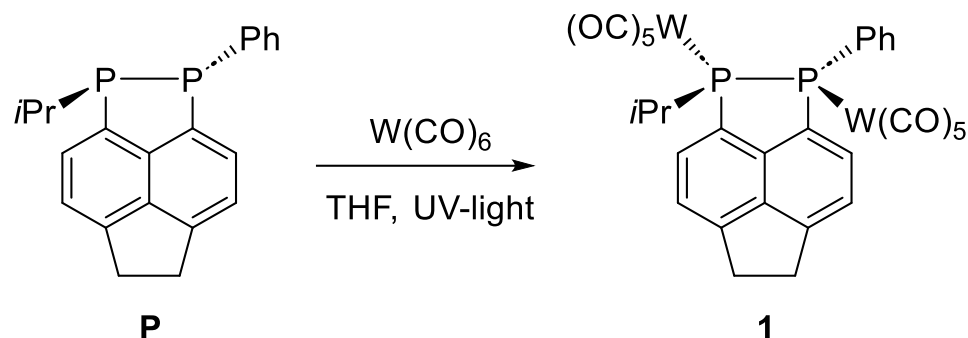
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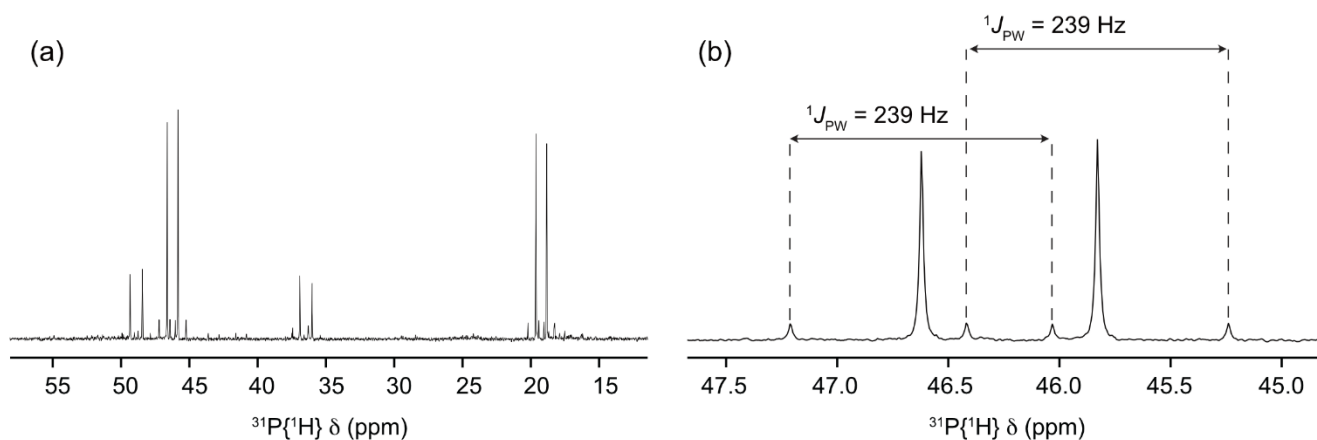
## 2. Results

An “unsymmetrical” derivative of **A**, bearing a rigid acenaphthene skeleton and two different substituents at phosphorus atoms, **P**, was synthesized by Kilian *et al.* via the dealkanative P–P coupling of bis(phosphines) [4]. The 1,2-diphosphole **P** is exclusively formed as the *trans* isomer from the dealkanative coupling. The synthesis of **1** involves a one-pot reaction where **P** and  $W(CO)_6$  are dissolved in THF and stirred under UV irradiation (365 nm) for 24 h (Scheme 1). After work-up, **1** was isolated and characterized, including the structure of *trans*-**1**, which was solved by X-ray crystallography.



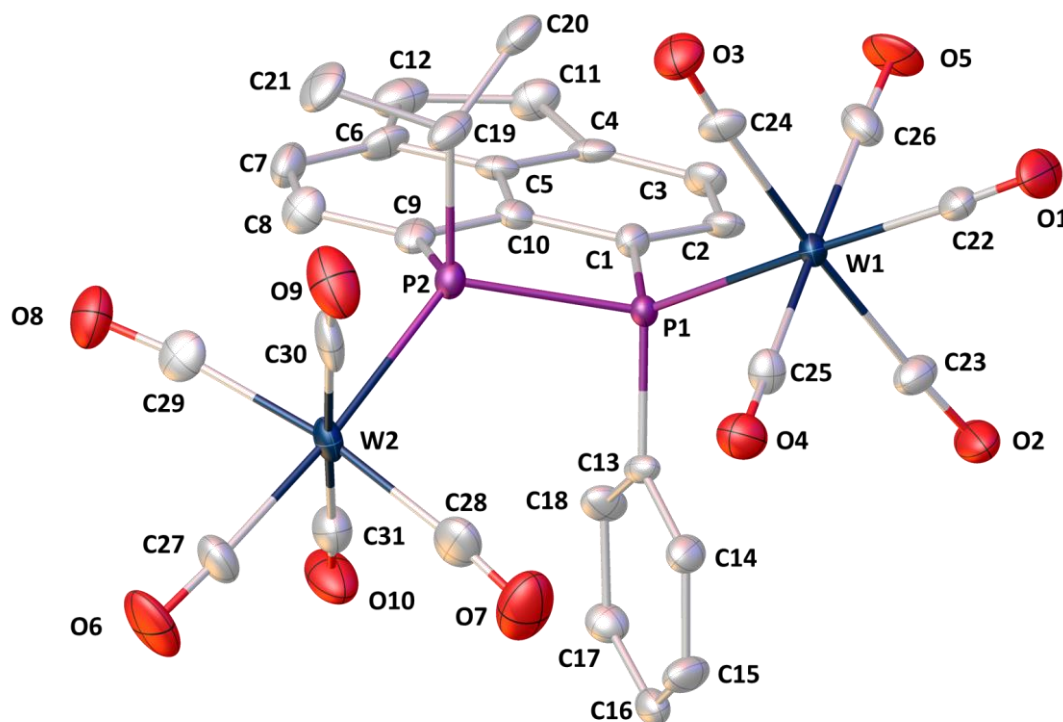
**Scheme 1.** Synthesis of compound (*trans*-**1**) by coordination of the asymmetric 1,2-diphosphole (**P**) to two  $W(CO)_5$  groups.

The  $^{31}P\{^1H\}$  NMR spectrum of **1**, shown in Figure 2a, indicates the formation of two products in an approximately 85:15 ratio. These products give rise to signals at  $\delta_P$  58.9 and 36.5 ppm ( $^1J_{PP}$  182 Hz) and 46.2 and 19.2 ppm ( $^1J_{PP}$  161 Hz). Further irradiation of the products with UV light results in no changes in the relative peak intensities. Tungsten has one NMR active isotope  $^{183}W$  ( $I = \frac{1}{2}$ ), which has a natural abundance of 14.31%.  $^{183}W$  satellite peaks can be observed for each of the four phosphorus resonances, with  $^1J_{PW}$  varying from 232 Hz to 303 Hz, indicating that both products have both phosphorus atoms coordinated to tungsten. This suggests that a mixture of the *trans* and *cis* isomers of compound **1** have formed, with the most dominant product likely being that of *trans*-**1**. This is expected given the increased steric strain in the *cis* isomer and is supported by the findings of Muzuta *et al.* with their work on the naphthalene derivative. As the standard P–P bond is relatively weak (*ca.* 255 kJ/mol) [5], it is likely that the UV irradiation of the ligand during the reaction enables the cleavage of this bond, causing the observed isomerization.



**Figure 2.** (a) The  $^{31}P\{^1H\}$  NMR spectrum of compound **1**, showing the presence of two products, the *trans*-**1** (major) and *cis*-**1** (minor). (b) Expansion of the phosphorus resonance (arising from *trans*-**1**) at  $\delta_P$  46.2 ppm, showing satellite peaks corresponding to the  $^1J_{PW}$  coupling of 239 Hz. Full NMR spectra are available in the Supplementary Information, Figures S1–S4.

Crystals suitable for X-ray diffraction were grown from a solution in acetonitrile at 5 °C. The crystal structure revealed that of the two isomers present in the bulk, *trans*-1 crystallised. The structure of the (*R,R*) enantiomer of 1 is shown in Figure 3. There are a pair of crystallographically identical enantiomers, (*R,R*)-1 and (*S,S*)-1, in the solid-state structure. Selected bond lengths and angles are provided in Table 1 and selected crystallographic data are presented in Table S1 (Supplementary Information). There is no significant change in the splay angle of *trans*-1 compared with the free ligand (**P**). There is, however, a slight increase in the P–P bond length to 2.261(6) Å (from 2.232(2) Å), suggesting that some electron density is removed from the phosphorus atoms on coordination [4].



**Figure 3.** Molecular structure of (*R,R*)-1. Hydrogen atoms are omitted for clarity. Anisotropic displacement ellipsoids are set at the 50% probability level.

**Table 1.** Selected lengths (Å) and angles (°) for *trans*-1.

Peri-Region Bond Lengths		Peri-Region Bond Angles	
P1–P2	2.261(6)	C <sub>Ph</sub> –P1–W1	115.3(5)
P1–W1	2.532(3)	C <sub>iPr</sub> –P2–W2	117.2(5)
P2–W2	2.501(4)	P1–P2–W2	120.7(2)
W1...W2	5.856(1)	P2–P1–W1	123.6(2)
		Splay angle <sup>(a)</sup>	−8(1)
Out-of-plane displacements <sup>(b)</sup>		Dihedral angles	
P1	0.098	P1–C1...C9–P2	10.1(6)
P2	0.197	C1–C10...C5–C6	177(1)

<sup>(a)</sup> Sum of the three *peri*-angles—360°. <sup>(b)</sup> Measured from the mean plane of the C<sub>12</sub> acenaphthene backbone.

Both the P–C bond lengths and the P–P–C bond angles remain unchanged compared to free ligand (**P**). There is a slight increase in the out-of-plane displacement of both *peri*-substituted groups, with one atom displaced by 0.098 Å and the other by 0.197 Å. This is a result of the steric repulsion between the two W(CO)<sub>5</sub> groups and the acenaphthene backbone, which retains its rigidity with minimal twisting (C1–C10–C5–C6 of 177(1)°). The two P–W bond distances of 2.501(4) and 2.532(3) Å are as expected, and are very similar to those of *trans*-**B** [6]. Both tungsten atoms sit in an octahedral environment with minimal distortions, although some of the C≡O bonds in the carbonyl ligands that

are *cis* to the 1,2-diphosphole are bent away from the ligand to reduce steric strain (e.g.,  $W2-C28-O7 = 174.2(18)^\circ$ ). Both phosphorus atoms sit in distorted tetrahedral environments. Despite multiple attempts, we were unable to obtain a crystal structure of the second compound present in the bulk, which we propose is the *cis* isomer.

### 3. Materials and Methods

#### 3.1. General Considerations

All synthetic manipulations were performed under an atmosphere of dry nitrogen using standard Schlenk techniques or under an argon atmosphere in a Saffron glove box. All glass apparatus were stored in a drying oven (*ca.* 120 °C) prior to use. Dry solvents were collected from an MBraun solvent purification system and stored over appropriate molecular sieves. Water used in experiments was subject to nitrogen sparging and stored under nitrogen prior to use. Chemicals were taken from the laboratory inventory and used without further purification. Compound **P** was prepared according to the published method [4].

All NMR spectra were recorded using a Bruker Avance III (500 MHz) spectrometer at 25 °C. Assignments of  $^1\text{H}$  and  $^{13}\text{C}$  spectra were made in conjunction with appropriate 2D spectra. For  $^1\text{H}$  and  $^{13}\text{C}$  NMR, tetramethylsilane was used as an external standard. For  $^{31}\text{P}$  NMR, 85%  $\text{H}_3\text{PO}_4$  in  $\text{D}_2\text{O}$  was used as the external standard. Residual solvent peaks were also used for calibration ( $\text{CDCl}_3$   $\delta_{\text{H}}$  7.260 ppm;  $\delta_{\text{C}}$  77.160 ppm). Chemical shifts ( $\delta$ ) are given in parts per million (ppm). Coupling constants ( $J$ ) are quoted in Hertz (Hz).

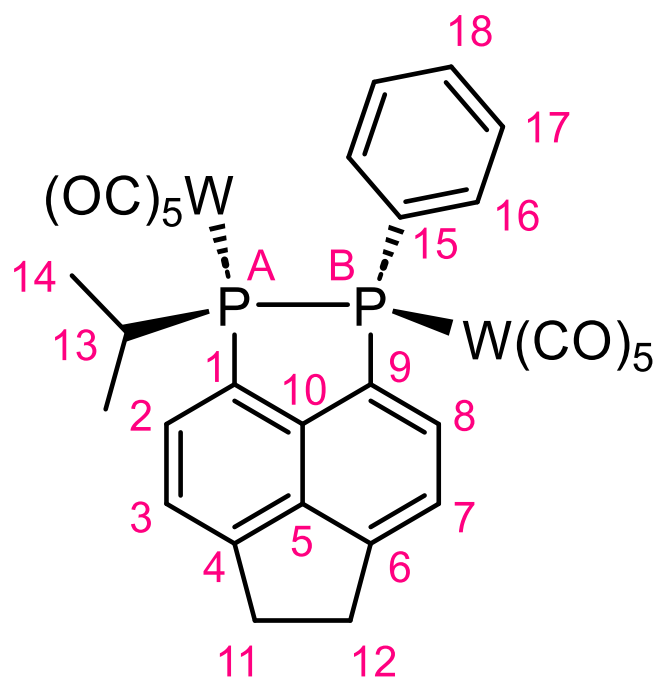
Melting and decomposition points were determined by heating solid samples in sealed glass capillaries using a Stuart SMP30 melting point apparatus. Mass spectrometry was performed at the EPSRC UK National Mass Spectrometry Facility in Swansea using a Finnigan MAT 95 XP (EI). Elemental analysis was performed by the EA Service at London Metropolitan University. Raman spectra were recorded on solid samples in glass capillaries using a Perkin-Elmer System 2000 NIR Fourier transform spectrometer with a dipole-pumped NdYAG laser, ranging between 30 and 150 mW power with a scanning range of 3500–100  $\text{cm}^{-1}$ .

#### 3.2. Synthetic Procedure

Synthesis of (Decacarbonyl)(1-isopropyl-2-phenyl-1,2,5,6-tetrahydroacenaphtho[5,6-cd][1,2]diphosphole)ditungsten(0) (**1**)

1-isopropyl-2-phenyl-1,2,5,6-tetrahydroacenaphtho[5,6-cd][1,2]diphosphole, **P**, (300 mg, 0.89 mmol) and tungsten hexacarbonyl (663 mg, 1.88 mmol) were dissolved in tetrahydrofuran (100 mL) and irradiated with a 6 W Hg UV lamp for 24 h. Irradiation of  $\text{W}(\text{CO})_6$  in THF produced  $\text{W}(\text{CO})_5(\text{THF})$  in situ. Volatiles were removed in vacuo and excess  $\text{W}(\text{CO})_6$  was removed by vacuum sublimation at 60 °C for 3 h, affording product **2**, a mixture of *cis*- and *trans* isomers as a yellow powder (470 mg, 54%) (M.p. 163–166 °C). Anal calcd. for  $\text{C}_{31}\text{H}_{20}\text{P}_2\text{W}_2\text{O}_{10}$ : C, 37.91; H, 2.05. Found: C, 38.04; H, 2.29. Raman: (glass capillary,  $\text{cm}^{-1}$ )  $\nu = 3069\text{m}$  ( $\nu$  CH), 2936s ( $\nu$  CH), 2078w, 1986vs ( $\nu$  C=O), 1914m ( $\nu$  C=O), 1609m ( $\nu$  C-C), 1448m ( $\nu$  C-C), 1419m ( $\nu$   $\text{CH}_2$ ), 1385m ( $\nu$   $\text{CH}_3$ ), 1030m, 1004m, 867m, 597m, 436s. HRMS (EI):  $\text{C}_{28}\text{H}_{20}\text{P}_2\text{W}_2\text{O}_7^+$  ( $\text{M}-3\text{CO}$ ) $^+$  calculated 897.970, found 897.971;  $\text{C}_{25}\text{H}_{20}\text{P}_2\text{W}_2\text{O}_4^+$  ( $\text{M}-6\text{CO}$ ) $^+$  calculated 813.9855, found 813.9862;  $\text{C}_{23}\text{H}_{20}\text{P}_2\text{W}_2\text{O}_2^+$  ( $\text{M}-\text{W}(\text{CO})_8$ ) $^+$  calculated 574.0448, found 574.0448;  $\text{C}_{21}\text{H}_{20}\text{P}_2\text{W}^+$  ( $\text{M}-\text{W}(\text{CO})_{10}$ ) $^+$  calculated 518.0550, found 518.0546;  $\text{C}_{21}\text{H}_{21}\text{P}_2$  ( $\text{M} + \text{H}-\text{W}_2(\text{CO})_{10}$ ) $^+$  calculated 335.1118, found 335.1122. The NMR numbering scheme is provided in Figure 4. Note, for  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, resonances are assigned for the *trans* isomer.  $^1\text{HMR}$ :  $\delta_{\text{H}}$  (500.1 MHz,  $\text{CDCl}_3$ ) 7.90 (1H, dd,  $^3J_{\text{HH}}$  7.6,  $^3J_{\text{HP}}$  7.6 Hz, H-8), 7.83 (1H, dd,  $^3J_{\text{HP}}$  9.3  $^3J_{\text{HH}}$  7.2 Hz, H-2), 7.63–7.60 (1H, m, H-7), 7.59 (1H, dd,  $^3J_{\text{HH}}$  7.2,  $^4J_{\text{HP}}$  2.3 Hz, H-3), 7.39–7.05 (5H, m, H-16–18) 3.63 (4H, s, H-11,12), 2.59 (1H, septd,  $^3J_{\text{HH}}$  6.7,  $^2J_{\text{HP}}$  6.7 Hz, H-13), 1.42 (3H, dd,  $^3J_{\text{HP}}$  20.0,  $^3J_{\text{HH}}$  6.9 Hz, H-14/14'), 0.71 (3H, dd,  $^3J_{\text{HP}}$  13.1,  $^3J_{\text{HH}}$  6.7 Hz, H-14/14').  $^{13}\text{C}\{^1\text{H}\}$  NMR:  $\delta_{\text{C}}$  (126 MHz,  $\text{CDCl}_3$ ) 196.4 (d,  $^2J_{\text{CP}}$  6.6 Hz, CO), 196.0 (d,  $^2J_{\text{CP}}$  6.9 Hz, CO), 149.8 (s, qC-6), 149.7 (s, qC-4), 138.4 (dd,  $^1J_{\text{CP}}$  5.9,  $^2J_{\text{CP}}$  5.9 Hz, qC-1), 134.7 (dd,  $^2J_{\text{CP}}$  12.0,  $^3J_{\text{CP}}$  2.2 Hz, C-16), 134.0 (d,  $^2J_{\text{CP}}$  10.4 Hz, C-8), 133.3 (d,  $^2J_{\text{CP}}$  11.9 Hz, C-2),

131.4 (s, qC-15), 131.2 (s, C-18), 128.8 (d,  $^3J_{CP}$  9.9 Hz, C-17), 121.7 (d,  $^3J_{CP}$  10.3 Hz, C-7), 121.5 (d,  $^3J_{CP}$  9.5 Hz, C-3), 34.9 (dd,  $^1J_{CP}$  14.0,  $^2J_{CP}$  7.8 Hz, C-13), 31.1 (s, C-11,12), 20.7 (dd,  $^2J_{CP}$  4.6,  $^3J_{CP}$  4.6 Hz, C-14/14'), 20.3 (dd,  $^2J_{CP}$  5.0 Hz,  $^3J_{CP}$  5.0 Hz, C-14/14').  $^{31}P\{^1H\}$  NMR:  $\delta_P$  (202.5 Hz,  $CDCl_3$ ) 48.9 (d with  $^{183}W$  satellites,  $^1J_{PP}$  182 Hz,  $^1J_{WP}$  303 Hz, P-*Acis*), 46.2 (d with  $^{183}W$  satellites,  $^1J_{PP}$  = 161 Hz,  $^1J_{WP}$  = 293 Hz, P-*Atrans*), 36.5 (d with  $^{183}W$  satellites,  $^1J_{PP}$  182 Hz,  $^1J_{WP}$  232 Hz, P-*Bcis*), and 19.2 (d with  $^{183}W$  satellites,  $^1J_{PP}$  160 Hz,  $^1J_{WP}$  235 Hz, P-*Btrans*).



**Figure 4.** NMR numbering scheme for **1**.

Crystals of **1** suitable for single crystal X-ray diffraction were grown from acetonitrile at 5 °C. For X-ray crystallography, all data were collected at 125 K using the St Andrews Automated Robotic Diffractometer (STANDARD), consisting of a Rigaku sealed-tube generator, equipped with a SHINE monochromator (Mo K $\alpha$  radiation ( $\lambda$  = 0.71075 Å)), and a Saturn 724 CCD area detector, coupled with a Microglide goniometer head and an ACTOR SM robotic sample changer [7]. Intensity data were collected using  $\omega$  steps accumulating area detector images, spanning at least a hemisphere of reciprocal space. Data for all compounds analysed were collected and processed (including correction for Lorentz, polarization, and absorption) using CrystalClear [8]. Structures were solved by SHELXT and refined by full-matrix least-squares against  $F^2$  (SHELXL-2018/3) and expanded upon using Fourier techniques [9]. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined using a riding model. All calculations were performed using the CrystalStructure interface [10]. Images of structures were generated using OLEX-2 [11]. Selected crystallographic data are presented in Table S1.

#### 4. Conclusions

A binuclear tungsten(0) complex with an unsymmetric, rigid, 1,2-diphosphole ligand was synthesised and the *trans* isomer characterised by NMR spectroscopy and single crystal X-ray diffraction as a pair of (*R,R*) and (*S,S*) enantiomers. The  $^{31}P\{^1H\}$  NMR spectrum shows coupling between  $^{31}P$  and  $^{183}W$  confirming both phosphorus atoms in the ligand are coordinated by pentacarbonyltungsten(0) groups.

**Supplementary Materials:** The following supporting information can be downloaded online. Figures S1–S4: NMR spectra of **1**; Table S1: Selected crystallographic data.

**Author Contributions:** Z.H.D. and L.J.T. carried out the required synthetic steps and preliminary analysis. C.L.C.-W. collected the X-ray data and solved the structures. B.A.C. and Z.H.D. collected and carried out the analysis of the other spectroscopic data. P.K. and B.A.C. designed the study, analysed the data, and wrote the manuscript. Z.H.D., B.A.C., P.K. and A.M.Z.S. provided supervision and laboratory equipment. All authors have read and agreed to the published version of the manuscript.

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**Data Availability Statement:** CCDC 2264466 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/structures](http://www.ccdc.cam.ac.uk/structures).

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**Conflicts of Interest:** The authors declare no conflict of interest.

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