

Synthesis of 1-phosphinophospholes and their tungstenpentacarbonyl complexes

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Abstract

A series of 1-phosphinophospholes **4a–d** (R = *tert*-butyl (**a**), *iso*-propyl (**b**), ethyl (**c**), phenyl (**d**)) and their pentacarbonyltungsten complexes **5a–d** are synthesized and characterized. The ³¹P NMR patterns of both the complexed and free 1-phosphinophospholes follow similar trends. The X-ray structure of **5a** reveals an elongated P–P bond due to steric encumbrance, while the geometry of the phosphole moiety is not affected.

Keywords: Phosphorus chemistry; Diphosphane; Diphosphane tungsten complex; Phosphinophosphole; Phosphinophosphole tungsten complex; X-ray

1. Introduction

Phosphole is the phosphorus analogue of the classic aromatic five-membered heterocycles pyrrole, furan, and thiophene. Numerous phosphole derivatives have been prepared with a wide spectrum of substituents at the various ring positions. The rapid development of phosphole chemistry has recently been reviewed [1]. Transition metal complexation of the phosphorus atom adds an extra dimension to the chemistry of phospholes [2]. An interesting application, developed by Marinetti and Mathey, is the Diels–Alder reaction of transition metal (M) complexed 1-R-3,4-dimethylphosphole with dimethyl acetylenedicarboxylate to give 7-phosphanorbornadienes, which are precursors to terminal phosphinidene complexes (R–P–M) [3]. These reactive, low coordinate phosphorus, carbene-like intermediates add to a plethora of double and triple bonded species, thereby expanding the area of small phosphorus heterocycles [4]. Incipient W(CO)₅ complexed phospholes have been generated with alkyl [5], aryl [6], alkoxy [7], and amino [8] substituents at the phosphorus, but none with a PR₂ substituent, although a 2-(diphenylphos-

phino)-phosphole has been synthesized [9]. We decided to explore the potential for PR₂ substituted phosphinidenes by investigating the synthesis of PR₂ substituted phospholes as a first step.

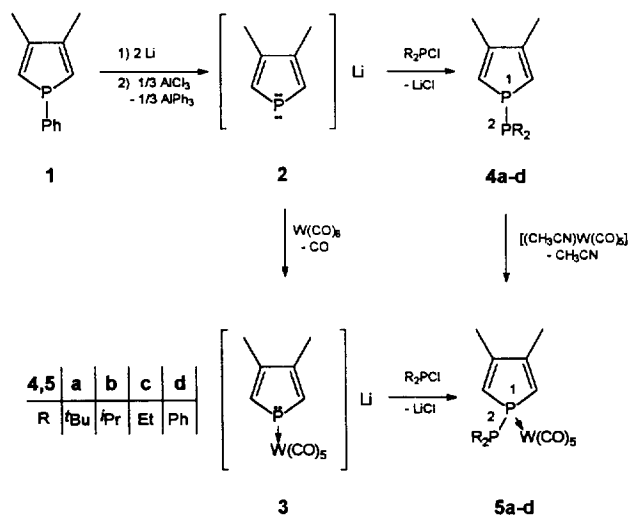
A large spectrum of diphosphanes (R₂P–PR) and their transition metal complexes is known. These have been comprehensively reviewed [10]. Many of the symmetrically substituted diphosphanes have been studied in detail [11–13], but less information is available on those systems containing phospholyl groups. Mathey and coworkers reported on the synthesis of symmetrical 1,1'-biphospholyls from pyrolysis (230 °C, 10 days) of 1-phenylphosphole [14]. This mechanism includes a 1,5-shift of the P-phenyl group [15]. Such sigmatropic shifts are common for phospholes [1]. Gentler routes are required for the synthesis of phosphinophospholes. The synthetic methodology of the phospholyl anion, developed by Holand et al. [16], provides a perfect entry into these systems. In their approach the anion is typically generated from 1-phenylphosphole by reduction using Li metal. The anion is then conveniently substituted at the phosphorus. For more sensitive substrates this step is performed in the coordination sphere of tungsten [17]. In this manner, phospholes have been substituted at phosphorus with alkyl [18,19], alkoxy [7], amino [8], aryl, carboxyl [10,20], cyano [20], halo [7], silyl [16], and stannyl [16] groups. Here we report on a similar

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approach towards the synthesis of the 1-phosphinophospholes **4** and their $W(CO)_5$ complexes **5**.

2. Results and discussion

The phospholyl anion **2** is conveniently generated from 1-phenyl-3,4-dimethylphosphole by the procedure developed by Holand et al. [16]. Nucleophilic attack of this anion on the chlorophosphanes R_2PCl ($R = Et, ^iPr, ^tBu,$ and Ph) affords the uncomplexed 1-phosphinophospholes **4a–d** in good yields. These substances are thermolabile and sensitive towards air and moisture. They can be isolated under inert conditions as white to pale yellow wax-like materials, and stored at $-30^\circ C$ for several weeks. Reaction of the phospholide anion **2** with an equimolar amount of tungsten hexacarbonyl gives the η^1 -complex **3** [17]. This complex reacts with the chlorophosphanes R_2PCl to give the η^1 -complexes **5a–d** in moderate yields. These complexes were obtained as light yellow solids after column chromatography. Reaction of the free ligands **4a–d** with acetonitrile-tungstenpentacarbonyl also gives **5a–d**, but with formation of more side products. The ^{31}P NMR characteristics of **4a–d** and **5a–d** are summarized in Table 1.



A single crystal structure determination was obtained for **5a** for evaluation of its geometrical parameters and comparison with reported diphosphanes.

The assignment of ^{31}P NMR chemical shifts is based on the ^{183}W -satellites of the phosphole P(1) of the $W(CO)_5$ complexed compounds **5a–d**. These P(1)-nuclei all show characteristically large couplings, $^2J_{P-H} = 36.6$ to 38.6 Hz, with the protons on the α -carbon atoms of the phosphole ring, which are common for phospholes of this type, e.g. for **1**, $^2J_{PH} = 38.3$ Hz.

Table 1
 ^{31}P NMR chemical shifts (ppm) and coupling constants (Hz) for **4a–d** and the $W(CO)_5$ complexed **5a–d**

Compound	$\delta P(2)$	$\delta P(1)$	$\Delta \delta(P2 - P1)$	$^1J_{P-P}$
4a (tBu)	34.8	-18.5	53.3	388.0
4b (iPr)	8.7	-23.8	32.5	327.9
4c (Et)	-20.3	-17.3	3.0	281.1
4d (Ph)	-8.7	-21.7	13.0	230.4
5a	65.3	-31.2	96.8	270.1
5b	30.1	-16.5	46.6	242.8
5c	-6.0	-8.9	2.6	238.7
5d	1.8	-8.6	10.4	249.2

Since the P(1) atoms in **4a–d** exhibit similar coupling constants, $^2J_{P-H} = 31.4$ to 39.0 Hz, their resonances were assigned accordingly.

2.1. Chemical shifts

The differences in ^{31}P NMR chemical shifts for the phosphane P atoms P(2) are significant. They amount to 55 ppm for the uncomplexed **4a–d** (range 34.8 to -20.3 ppm) and to an even larger 71 ppm for the $W(CO)_5$ complexed compounds **5a–d** (range 65.3 to -6.0 ppm). For the phosphole P atoms P(1) these differences in chemical shift are much less pronounced: only 5.5 ppm for **4a–d** (range -17.3 to -23.8 ppm) and 22.6 ppm for **5a–d** (range -8.6 to -31.2 ppm). The phosphole P(1) is more shielded than the phosphane P(2) in all cases but **4c**.

The ^{31}P NMR chemical shifts and coupling constants for **4a–d** and **5a–d** fall in the range expected for diphosphanes [10–12] and biphospholyls [14]. It is instructive to make comparisons, particularly with respect to the size of the phosphine substituents. In both the series **4** and **5**, the resonance of P(2) becomes increasingly more deshielded as its substituents increase in size in the order $Et \rightarrow Ph \rightarrow ^iPr \rightarrow ^tBu$. The increase in steric demand of the substituent widens the CPC bond angle and thereby enhances the s-character of the hybridization of P(2), which results in a deshielding effect. This effect is more pronounced in the series **5a–d**, where the neighboring $W(CO)_5$ group increases the crowding at P(2). Comparable steric influences have been reported for the symmetrical diphosphanes P_2R_4 [10], which have $\delta(^{31}P)$ values of -32.7 ($R = Et$) [11], -14.1 ($R = Ph$) [11], -11.6 ($R = ^iPr$) [13], and $+40.0$ ppm ($R = ^tBu$) [13]. In contrast, the ^{31}P NMR chemical shifts of the phosphole P(1) nucleus in **4a–d** show no dependence on the size of the P(2) R_2 substituents ($\delta_{av} P(1) = -20.3$ ppm), which suggests that its hybridization is not effected. As expected, there is a small shielding effect in the series **5a–d**, which is due to the increased crowding at P(1) resulting from the additional transition metal group.

2.2. Coupling constants

The phosphorus–phosphorus coupling constants in diphosphanes are known to have negative values [11,12]. Substituent effects influence the magnitude of $^1J_{P-P}$ significantly. Bulkier substituents widen the CP(2)C bond angle, which enhances the s-character of the P–C bonds with a concomitant reduction in the P–P bond length, resulting in a larger $^1J_{P-P}$ [13,21]. For example, the $^1J_{P-P}$ values for the symmetrical diphosphanes are 108 Hz for P_2H_4 , 179.7 Hz for P_2Me_4 , 221 Hz for P_2Et_4 , 302 Hz for $P_2^iPr_4$ and 449 Hz for $P_2^tBu_4$ [13,22]. Although the differences in $^1J_{P-P}$ values for the series **4a–d** are substantial (range 230–388 Hz), they are slightly less pronounced than for the P_2R_4 diphosphanes. This must be attributed to the electronically different behavior of the aromatic phosphole and the PR_2 group; phosphorus lone pairs are known to enhance the negative value of $^1J_{P-P}$ [13]. However, the trends are the same, that is the larger $^1J_{P-P}$ values are found for the sterically more congested systems [13]. Similar trends are observed for **5a–d**, but for these systems the differences in $^1J_{P-P}$ are very modest with a range of only 239–270 Hz, which is a result of the higher coordination of the phosphole P(1).

The $^1J_{PP}$ coupling constants show the same trends as the ^{31}P chemical shifts and, as expected, both parameters correlate linearly for **4a**, **b**, and **c**. This illustrates the progressive steric effect of the Et, iPr , and tBu groups on the CPC bond angle. Such a $^1J_{PP} - \delta P(2)$ relationship is not evident for **5a**, **b**, and **c**, which instead show a correlation between their P(2) and P(1) chemical shifts. Both the PPh_2 derivatives **4d** and **5d** show ^{31}P NMR chemical shifts and $^1J_{PP}$ coupling constants that resemble those of the PEt_2 derivatives best; it has been argued that the π -delocalization in phenylphosphanes is not important [23].

2.3. Single crystal X-ray structure

To further explore the steric demands in these compounds we decided to obtain a single crystal X-ray structure determination for the most crowded system, **5a**. Its structure is shown in Fig. 1 and the X-ray crystallographic data are summarized in Table 2. Bond lengths and selected angles are listed in Tables 3 and 4 respectively. Coordinates and equivalent isotropic thermal parameters of **5a** are given in Table 5. The most relevant features are the P–P bond lengths, the CPC bond angles, and the conformation. The P(1)–P(2) bond distance of 2.250(2) Å is rather long compared with the usual lengths of 2.19 to 2.22 Å [24]. This confirms the interpretation of the NMR data. The bond angle between the two tBu groups, i.e. C(12)–P(2)–C(16), of 110.8(3)° is also significantly larger than, for example, the ca. 99° CPC angle in PMe_3 and ca. 103° in PPh_3

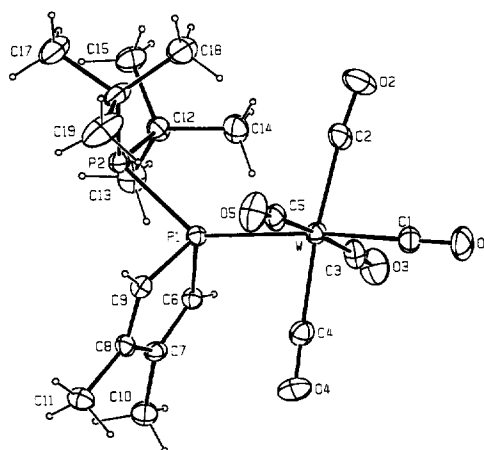


Fig. 1. ORTEP plot of the phosphinophosphole complex **5a**.

[25]. Interestingly, the phosphole ring is in a *trans* conformation to the two tBu groups of P(2). In other words, the $W(CO)_5$ group complexed to P(1) is *trans* to the lone pair of P(2). Such conformations have been reported for other less crowded complexed diphosphanes. The planar phosphole ring with its ‘normal’ C(6)–P(1)–C(9) bond angle of 89.5(3)° shows no signs of ring strain. Also, the P(1)–W bond length of 2.572(2)

Table 2
Data collection and refinement parameters

Formula	$C_{19}H_{26}O_5WP_2$
Color/shape	yellow fragment
Formula weight	580.2
Space group	<i>Pbca</i>
Cell constants	
<i>a</i> (Å)	9.9942(9)
<i>b</i> (Å)	16.5954(11)
<i>c</i> (Å)	28.680(4)
Cell volume (Å ³)	4757(2)
Formula units/unit cell	8
D_{calc} (g cm ⁻³)	1.620
μ_{calc} (cm ⁻¹)	51.2
Diffractometer/scan	Enraf–Nonius CAD4/ $\omega-2\theta$
Radiation, graphite monochromated	Mo K α ($\lambda = 0.71073$ Å)
Max. crystal dimensions (mm ³)	0.22 × 0.35 × 0.45
No. standard reflections	3
Decay of standards	3.8%
Relative transmission coefficients	0.793–0.999
2 θ range (°)	2 < 2 θ < 55
Octants collected	<i>hkl</i>
Reflections measured	6059
Independent reflections	5434
Reflections observed	3438
Criterion for observed reflections	$I > 1\sigma(I)$
No. of parameters varied	245
Weights	$4F_{o2}[\sigma^2(I) + (0.02F_{o2})^2]^{-1}$
$R = \Sigma F_o - F_c / \Sigma F_o $	0.044
R_w	0.034
Extinction coefficient	$4.4(1) \times 10^{-8}$
Max. shift/e.s.d.	0.09
Largest feature in final difference map	$0.74 e \text{ \AA}^{-3}$

Table 3
Bond lengths (Å) for **5a**

W–P(1)	2.572(2)	O(4)–C(4)	1.144(9)
W–C(1)	1.995(7)	O(5)–C(5)	1.144(9)
W–C(2)	2.008(7)	C(6)–C(7)	1.320(9)
W–C(3)	2.023(7)	C(7)–C(8)	1.477(8)
W–C(4)	2.023(7)	C(7)–C(10)	1.50(1)
W–C(5)	2.018(7)	C(8)–C(9)	1.336(8)
P(1)–P(2)	2.250(2)	C(8)–C(11)	1.494(9)
P(1)–C(6)	1.797(6)	C(12)–C(13)	1.54(1)
P(1)–C(9)	1.787(6)	C(12)–C(14)	1.52(1)
P(2)–C(12)	1.901(7)	C(12)–C(15)	1.53(1)
P(2)–C(16)	1.892(7)	C(16)–C(17)	1.53(1)
O(1)–C(1)	1.132(9)	C(16)–C(18)	1.53(1)
O(2)–C(2)	1.158(9)	C(16)–C(19)	1.51(1)
O(3)–C(3)	1.147(9)		

compares well with those of other $W(CO)_5$ complexed phospholes. The W–P(1)–P(2) bond angle of $137.51(8)^\circ$ is much wider than the comparable WPC angle of 120 – 125° in related complexes. This does suggest a steric repulsion between the $W(CO)_5$ and the P^iBu_2 groups. It is evident that the crystal structure of **5a** fully confirms the interpretations of the ^{31}P NMR data.

2.4. Conclusion

Phosphinophospholes and their $W(CO)_5$ complexes are synthesized with remarkable ease. Substitution of the phosphane phosphorus and transition metal complexation influence the P–P bonding. This is reflected in the ^{31}P NMR parameters and is evident from an X-ray structure of **5a**. While **5a** is of significant stability it does not give phosphino substituted 7-phosphanorbornadienes by means of a Diels–Alder reaction with dimethyl acetylenedicarboxylate. Its P–P bond does not survive the reaction conditions for the thermal cycloaddition of the phosphole ring. This is not surprising, since even the amino and alkoxy substituted 7-phos-

Table 4
Selected bond angles ($^\circ$) for **5a**

P(1)–W–C(1)	174.5(2)	C(8)–C(7)–C(10)	119.9(6)
P(1)–W–C(2)	100.2(2)	C(7)–C(8)–C(9)	112.1(5)
P(1)–W–C(3)	89.2(2)	C(7)–C(8)–C(11)	123.1(6)
P(1)–W–C(4)	84.5(2)	C(9)–C(8)–C(11)	124.8(6)
P(1)–W–C(5)	89.5(2)	P(1)–C(9)–C(8)	112.5(4)
W–P(1)–P(2)	137.51(8)	P(2)–C(12)–C(13)	104.3(5)
W–P(1)–C(6)	109.7(2)	P(2)–C(12)–C(14)	115.4(5)
W–P(1)–C(9)	110.3(2)	P(2)–C(12)–C(15)	110.8(5)
P(2)–P(1)–C(6)	100.2(2)	C(13)–C(12)–C(14)	108.5(6)
P(2)–P(1)–C(9)	99.1(2)	C(13)–C(12)–C(15)	107.1(6)
C(6)–P(1)–C(9)	89.5(3)	C(14)–C(12)–C(15)	110.3(6)
P(1)–P(2)–C(12)	104.3(2)	P(2)–C(16)–C(17)	107.0(5)
P(1)–P(2)–C(16)	103.8(2)	P(2)–C(16)–C(18)	117.7(5)
C(12)–P(2)–C(16)	110.8(3)	P(2)–C(16)–C(19)	105.8(5)
P(1)–C(6)–C(7)	111.5(4)	C(17)–C(16)–C(18)	109.8(6)
C(6)–C(7)–C(8)	114.4(5)	C(17)–C(16)–C(19)	106.2(6)
C(6)–C(7)–C(10)	125.7(6)	C(18)–C(16)–C(19)	109.7(6)

Table 5
Coordinates and equivalent isotropic thermal parameters for **5a**

Atom	x	y	z	B_{eq} (\AA^2)
W	0.58727(3)	0.22625(2)	0.14289(1)	4.046(5)
P(1)	0.4867(2)	0.3545(1)	0.10678(6)	3.61(3)
P(2)	0.3074(2)	0.4340(1)	0.11832(6)	4.04(4)
O(1)	0.7257(6)	0.0684(3)	0.1778(2)	8.5(2)
O(2)	0.4099(6)	0.2037(3)	0.2333(2)	8.8(2)
O(3)	0.7822(6)	0.3377(3)	0.2016(2)	8.7(2)
O(4)	0.7943(5)	0.2348(4)	0.0594(2)	8.7(2)
O(5)	0.4064(6)	0.1198(3)	0.0768(2)	9.2(2)
C(1)	0.6763(7)	0.1259(4)	0.1654(2)	5.6(2)
C(2)	0.4707(8)	0.2147(4)	0.1995(3)	5.7(2)
C(3)	0.7120(7)	0.2958(4)	0.1812(2)	5.7(2)
C(4)	0.7195(7)	0.2331(4)	0.0896(2)	5.5(2)
C(5)	0.4681(7)	0.1590(4)	0.1015(2)	5.4(2)
C(6)	0.6150(6)	0.4295(4)	0.1002(2)	3.9(1)
C(7)	0.6466(6)	0.4404(4)	0.0559(2)	4.2(1)
C(8)	0.5679(6)	0.3912(4)	0.0230(2)	4.1(1)
C(9)	0.4780(6)	0.3451(4)	0.0448(2)	3.8(1)
C(10)	0.7539(8)	0.4957(5)	0.0380(3)	6.6(2)
C(11)	0.5875(8)	0.3943(5)	–0.0287(2)	6.1(2)
C(12)	0.3425(7)	0.4861(4)	0.1761(2)	5.1(2)
C(13)	0.4183(9)	0.5635(5)	0.1624(3)	7.1(2)
C(14)	0.4288(8)	0.4386(5)	0.2102(2)	7.1(2)
C(15)	0.2123(8)	0.5122(5)	0.1995(3)	7.9(2)
C(16)	0.1639(6)	0.3604(4)	0.1243(3)	5.8(2)
C(17)	0.0343(8)	0.4095(5)	0.1213(3)	8.1(3)
C(18)	0.1609(9)	0.3065(5)	0.1677(4)	9.9(3)
C(19)	0.1680(8)	0.3088(5)	0.0810(4)	9.9(3)

$$B_{eq} = 8\pi^2 / 3 \sum_i \sum_j \mu_{ij} a_i^* a_j \cdot a_j$$

phanorbornadienes are synthesized with difficulty. The information obtained about the methodology of synthesizing asymmetric diphosphanes is valuable and awaits applications in synthetic schemes that are currently underway in our laboratories.

3. Experimental section

NMR spectra were recorded on a Bruker NT-300 wide bore and a Bruker ARX-300 FT-NMR spectrometer at 300.1 MHz for 1H , 75.45 MHz for ^{13}C , and 121.496 MHz for ^{31}P at 298 K. Chemical shifts are referenced in parts per million to internal $Si(CH_3)_4$ for 1H and ^{13}C and external 85% H_3PO_4 for ^{31}P . Downfield shifts are reported as positive. Unless stated otherwise, all NMR spectra were recorded in benzene- d_6 . IR spectra were recorded on a Nicolet IR44 spectrometer, mass spectra on a HP 5985 at 70 eV. All materials were handled with Schlenk and cannula techniques under argon. Reagents were used as purchased, solvents were dried using standard methods, oxygen free and distilled prior to use.

3.1. Lithium-3,4-dimethylphospholide 2

Prepared in a variation of the published procedure [26]. An excess of lithium ribbon was added to a

solution of 3,4-dimethyl-1-phenyl-phosphole **1** [27] in THF, and the progress of conversion into the lithium compound monitored by ^{31}P NMR (δ +55 ppm). Excess lithium was then removed, followed by usual work-up.

3.2. Lithium-[($\eta^1(\text{P})$)-3,4-dimethylphospholide]-pentacarbonyltungsten **3**

A solution of **2** in THF was treated with an equivalent amount of tungsten hexacarbonyl, and stirred overnight. After the conversion was complete, as confirmed by ^{31}P NMR, the solution was used immediately. ^{31}P NMR: δ -55, $^1J(^{31}\text{P}^{183}\text{W}) = 102.8$ Hz.

3.3. General procedure for the preparation of the 1-phosphinophospholes **4a–d**

A stirred solution of 2 mmol CIPR_2 ($\text{R} = ^t\text{Bu}$, 0.36 g; $\text{R} = ^i\text{Pr}$, 0.3 g; $\text{R} = \text{Et}$, 0.25 g; $\text{R} = \text{Ph}$, 0.62 g) in 20 ml ether was cooled to -60°C and treated dropwise with a solution of 2 mmol **2** in 50 ml THF. The mixture was allowed to warm to ambient temperature and stirred overnight. All volatiles were removed in vacuo. The residue was extracted with 200 ml of hexanes, and filtered through a bed of Celite. The solution was concentrated in vacuum and cooled to -25°C . The precipitate was removed, and the remaining solution dried in vacuo.

3.3.1. 1-(Di-tert-butylphosphino)-3,4-dimethyl-phosphole **4a**

Pale yellow solid, m.p. 48°C . Yield 0.36 g (70%). ^{31}P NMR: δ 34.8 (dm, $^1J_{\text{PP}} = 388.0$ Hz, $^3J_{\text{PH}} = 12.0$ Hz, $^t\text{Bu}_2\text{P}$); -18.5 (dt, $^1J_{\text{PP}} = 388.0$ Hz, $^3J_{\text{PH}} = 38.3$ Hz, $^t\text{Bu}_2\text{P-P}$). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 146.1 (dd, $^2J_{\text{CP}} = 1.9$ Hz, $^3J_{\text{CP}} = 9.8$ Hz, $\beta\text{-C}$); 129.8 (pseudo-t, $J_{\text{CP}} = 6.6$ Hz, $\alpha\text{-C}$); 35.9 (dd, $^1J_{\text{CP}} = 30.1$ Hz, $^2J_{\text{CP}} = 3.9$ Hz, $\text{C}(\text{CH}_3)_3$); 31.6 (dd, $^2J_{\text{CP}} = 13.2$ Hz, $^3J_{\text{CP}} = 5.4$ Hz, $\text{C}(\text{CH}_3)_3$); 18.3 (d, $^3J_{\text{CP}} = 3.9$ Hz, $\beta\text{-CH}_3$). ^1H NMR: δ 6.6 (d, $^2J_{\text{HP}} = 38.3$ Hz, 2H, $\alpha\text{-H}$); 1.85 (d, $^4J_{\text{HP}} = 1.8$ Hz, 6H, $\beta\text{-CH}_3$); 1.1 (d, $^3J_{\text{HP}} = 11.8$ Hz, 18H, $\text{C}(\text{CH}_3)_3$).

3.3.2. 3,4-Dimethyl-1-(di-iso-propylphosphino)-phosphole **4b**

Pale yellow semi-solid. Yield 0.28 g (61%). ^{31}P NMR: δ 8.7 (d, $^1J_{\text{PP}} = 327.9$ Hz, $^i\text{Pr}_2\text{P}$); -23.8 (dt, $^1J_{\text{PP}} = 327.9$ Hz, $^2J_{\text{PH}} = 38.6$ Hz, $^i\text{Pr}_2\text{P-P}$). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 147.8 (dd, $^2J_{\text{CP}} = 5.5$ Hz, $^3J_{\text{CP}} = 16.4$ Hz, $\beta\text{-C}$); 129.8 (d, $^1J_{\text{CP}} = 8.1$ Hz, $\alpha\text{-C}$); 25.1 (d, $^1J_{\text{CP}} = 21.0$ Hz, $\text{CH}(\text{CH}_3)_3$); 21.4 (d, $^2J_{\text{CP}} = 11.95$ Hz, $\text{CH}(\text{CH}_3)_2$); 18.3 (d, $^3J_{\text{CP}} = 3.4$ Hz, $\beta\text{-CH}_3$). ^1H NMR: δ 6.4 (d, $^2J_{\text{HP}} = 38.6$ Hz, 2H, $\alpha\text{-H}$); 1.85 (s, 6H, $\beta\text{-CH}_3$); 1.6 (sept, $^3J_{\text{HH}} = 7.0$ Hz, 2H, $\text{CH}(\text{CH}_3)_2$), 0.9 (m, $^3J_{\text{HH}} = 7.0$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$).

3.3.3. 1-(Diethylphosphino)-3,4-dimethyl-phosphole **4c**

White semi-solid. Yield 0.29 g (50%). ^{31}P NMR: δ -17.3 (dt, $^1J_{\text{PP}} = 281.1$ Hz, $^2J_{\text{PH}} = 31.4$ Hz, $\text{Et}_2\text{P-P}$); -20.3 (d [broadened], $^1J_{\text{PP}} = 281.1$ Hz, Et_2P). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 147.8 (pseudo-t, $J_{\text{CP}} = 4.4$ Hz, $\beta\text{-C}$); 126.8 (s, $\alpha\text{-C}$); 16.3 (d, $^2J_{\text{CP}} = 2.6$ Hz, $\beta\text{-CH}_3$); 17.3 (dd, $\Sigma(^2J_{\text{CP}} + ^3J_{\text{CP}}) = 21.3$ Hz, CH_2CH_3); 10.2 (dd, $\Sigma(^1J_{\text{CP}} + ^2J_{\text{CP}}) = 21.4$ Hz, CH_2). ^1H NMR: δ 6.44 (dd, $\Sigma(^2J_{\text{HP}} + ^3J_{\text{HP}}) = 38.9$ Hz, 2H, $\alpha\text{-H}$); 1.9 (s, 6H, $\beta\text{-CH}_3$); 1.32–1.52 (m, 4H, CH_2CH_3); 0.9–1.18 (m, 6H, CH_2CH_3).

3.3.4. 3,4-Dimethyl-1-(diphenylphosphino)-phosphole **4d**

Pale yellow amorphous semi-solid. Yield 0.18 g (30%). ^{31}P NMR: δ -8.7 (dm, $^1J_{\text{PP}} = 230.4$ Hz, Ph_2P); -21.7 (dt, $^1J_{\text{PP}} = 230.4$ Hz, $^2J_{\text{PH}} = 39.0$ Hz, $\text{Ph}_2\text{P-P}$). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 150.1 (pseudo-t, $J_{\text{CP}} = 4.0$ Hz, $\beta\text{-C}$); 136.2 (dd, $\Sigma(^2J_{\text{CP}} + ^3J_{\text{CP}}) = 31.2$ Hz, *ipso*-C); 133.3 (dd, $\Sigma(^3J_{\text{CP}} + ^4J_{\text{CP}}) = 25.9$ Hz, *m*-C); 127.3 (s, *p*-C); 134.6 (dd, $\Sigma(^1J_{\text{CP}} + ^2J_{\text{CP}}) = 26.7$ Hz, $\alpha\text{-C}$); 127.1 (pseudo-t, $J_{\text{CP}} = 2.8$ Hz, *o*-C); 16.2 (d, $^3J_{\text{CP}} = 2.8$ Hz, $\beta\text{-CH}_3$). ^1H NMR: δ 7.5–7.6 (m, 8H, Ph); 7.05–7.09 (m, 2H, *p*-Ph); 6.3 (d, $^2J_{\text{HP}} = 39.0$ Hz, 2H, $\alpha\text{-H}$); 1.17 (t, $^4J_{\text{HP}} = 2.2$ Hz, 6H, $\beta\text{-CH}_3$).

3.4. General procedure for the preparation of the 1-phosphinophosphole complexes **5a–d**

A solution of 10 mmol CIPR_2 ($\text{R} = ^t\text{Bu}$, 1.8 g; $\text{R} = ^i\text{Pr}$, 1.5 g; $\text{R} = \text{Et}$, 1.25 g; $\text{R} = \text{Ph}$, 0.32 g) in 20 ml ether was cooled to -70°C and treated dropwise with a solution of 10 mmol **3** in 50 ml THF. The reaction mixture was allowed to warm to room temperature and stirred for another 30 min. After removing all volatiles in vacuum, the residue was extracted with 200 ml of hexanes. The hexanes solution was flashed through a short silica gel column. After solvent removal in vacuo, yellow solids were obtained.

3.4.1. [$\eta^1(\text{P})$]-1-(Di-tert-butylphosphino)-3,4-dimethyl-phosphole]-pentacarbonyltungsten **5a**

Yellow crystals, m.p. 102°C . Yield 2.7 g (46%). ^{31}P NMR: δ 65.3 (dm, $^1J_{\text{PP}} = 270.1$ Hz, $^3J_{\text{PH}} = 14.2$ Hz, $^t\text{Bu}_2\text{P}$); -31.2 (dt, $^1J_{\text{PP}} = 270.1$ Hz, $^2J_{\text{PH}} = 38.8$ Hz, $^1J_{\text{PW}} = 189.2$ Hz, $^t\text{Bu}_2\text{P-P}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 198.7 (d, $^2J_{\text{CP}} = 19.5$ Hz, *cis*-CO); 197.8 (d, $^2J_{\text{CP}} = 7.6$ Hz, *trans*-CO); 149.1 (s, $\beta\text{-C}$); 133.7 (dd, $^1J_{\text{CP}} = 41.3$ Hz, $^2J_{\text{CP}} = 8.8$ Hz, $\alpha\text{-C}$); 34.4 (d, $^1J_{\text{CP}} = 36.2$ Hz, CMe_3); 31.2 (dd, $^2J_{\text{CP}} = 14.2$ Hz, $^3J_{\text{CP}} = 5.5$ Hz, CCH_3); 16.6 (d, $^3J_{\text{CP}} = 9.6$ Hz, $\beta\text{-CH}_3$). ^1H NMR (CDCl_3): δ 6.56 (d, $^2J_{\text{HP}} = 38.8$ Hz, 2H, $\alpha\text{-H}$); 2.22 (d, $^4J_{\text{HP}} = 2.0$ Hz, 6H, $\beta\text{-CH}_3$); 1.6 (dd, $^3J_{\text{HP}} = 11.0$ Hz, $^4J_{\text{HP}} = 1.5$ Hz, 18H, $\text{C}(\text{CH}_3)_3$). IR (film, CDCl_3): $\nu = 2068, 1936\text{ cm}^{-1}$. MS (*m/e*, relative intensity): 580 (M^+ , 2.8); 552 ($\text{M} - \text{CO}$, 3.5); 524 ($\text{M} - 2\text{CO}$, 4.0);

496 (M – 3CO, 5.2), 468 (M – 4CO, 12.2), 440 (M – 5CO, 10.0), 348 (PhPW(CO)₂, 50.5); 320 (PHPW(CO), 15.0); 292 (PhPW, 30.0).

3.4.2. [$\eta^1(P)$]-3,4-Dimethyl-1-(di- σ -propylphosphino)-phosphole]-pentacarbonyl tungsten **5b**

Yield 1.8 g (32%). ³¹P NMR: δ 30.1 (d, sept ¹J_{PP} = 242.8 Hz, ³J_{PH} = 13.4 Hz, ¹Pr₂P); –16.7 (dt, ¹J_{PP} = 242.8 Hz, ²J_{PH} = 38.4 Hz, ³J_{PH} = 10.2 Hz, ¹J_{PW} = 189.5 Hz, ¹Pr₂P–P). ¹³C{¹H} NMR (CDCl₃): δ 198.4 (d, ²J_{CP} = 19.6 Hz, *cis*-CO); 196.4 (d, ²J_{CP} = 4.8 Hz, *trans*-CO); 150.5 (s, β -C); 131.5 (dd, ¹J_{CP} = 30.9 Hz, ²J_{CP} = 4.6 Hz, α -C); 25.4 (d, ¹J_{CP} = 24.9 Hz, CHMe₂); 21.5 (d, ²J_{CP} = 13.4 Hz, CH(CH₃)₂); 16.3 (d, ³J_{CP} = 7.7 Hz, β -CH₃). ¹H NMR (CDCl₃): δ 6.2 (d, ²J_{HP} = 38.4 Hz, 2H, α -H); 2.9 (m, 2H, CHMe₂); 2.1 (d, ⁴J_{HP} = 2.5 Hz, 6H, β -CH₃); 1.35 (dd, ³J_{HP} = 3.4 Hz, ⁴J_{HP} = 2.0 Hz, 12H, CH(CH₃)₂).

3.4.3. [$\eta^1(P)$]-1-(Diethylphosphino)-3,4-dimethyl-phosphole]-pentacarbonyl tungsten **5c**

Yield 1.5 g (28%). ³¹P NMR: δ –6.3 (dt, ¹J_{PP} = 238.7 Hz, ¹J_{PH} = 36.6 Hz, ¹J_{PW} = 176.4 Hz, Et₂P–P); –8.9 (dm, ¹J_{PP} = 238.7 Hz, Et₂P). ¹³C{¹H} NMR (CDCl₃): δ 199.6 (d, ²J_{CP} = 15.9 Hz, *cis*-CO); 196.9 (d, ²J_{CP} = 4.9 Hz, *trans*-CO); 152.1 (dd, $\Sigma(^1J_{CP} + ^2J_{CP})$ = 7.3 Hz, β -C); 129.4 (dd, $\Sigma(^1J_{CP} + ^2J_{CP})$ = 38.2 Hz, α -C); 25.4 (dd, $\Sigma(^1J_{CP} + ^3J_{CP})$ = 25.6 Hz, CH₂CH₃); 18.5 (dd, $\Sigma(^1J_{CP} + ^2J_{CP})$ = 23.1 Hz, CH₂); 17.3 (d, ³J_{CP} = 9.9 Hz, β -CH₃). ¹H NMR: δ 6.1 (d, ²J_{HP} = 36.6 Hz, 2H, α -H); 1.7 (s, 6H, β -CH₃); 1.30 (m, 4H, CH₂); 0.95 (m, 6H, CH₂CH₃).

3.4.4. [$\eta^1(P)$]-3,4-Dimethyl-1-(diphenylphosphino)-phosphole]-pentacarbonyl tungsten **5d**

Yield 1.9 g (31%). ³¹P NMR: δ 1.8 (dm, ¹J_{PP} = 249.2 Hz, Ph₂P); –8.6 (dt, ¹J_{PP} = 249.2 Hz, ²J_{PH} = 38.6 Hz, ¹J_{PW} = 204.5 Hz, Ph₂P–P). ¹³C{¹H} NMR (CDCl₃): δ 196.6 (d, ²J_{CP} = 3.9 Hz, *trans*-CO); 152.9 (s, β -C); 135.1 (d, ¹J_{CP} = 19.3 Hz, α -C); 132.0–129.5 (m, aromatic C); 17.1 (d, ³J_{CP} = 10.2 Hz, β -CH₃). ¹H NMR (CDCl₃): δ 7.1–7.4 (m, 10H, aromatic H); 6.3 (d, ²J_{HP} = 38.6 Hz, 2H, α -H); 1.75 (s, 6H, β -CH₃).

3.5. X-ray data collection, structure determination, and refinement of **5a**

Intensity data were collected at room temperature by ω –2 θ scans of variable rate on an Enraf–Nonius CAD4 diffractometer equipped with graphite monochromated Mo K α radiation. The crystal was sealed in a capillary for data collection. Accurate unit cell parameters were obtained by least-squares refinement vs. $\sin \theta / \lambda$ values for 25 reflections having $11^\circ < \theta < 21^\circ$. The space group is uniquely determined by systematic absences. Data reduction included corrections for background, Lorentz,

polarization and absorption effects. Absorption corrections were based on ψ scans. The structure was solved by heavy-atom methods. Refinement was by full-matrix least-squares, with neutral-atom scattering factors and anomalous dispersion corrections, using the MolEN programs [28]. All non-hydrogen atoms were refined anisotropically, while H atoms were placed in calculated positions. Details of data collection and refinements are listed in Table 1.

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