Unusual diastereoselective reduction of 2-propionyl-3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene to the corresponding alcohol by $BH_3{\cdot}Me_2S$. X-Ray diffraction and DFT study†

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It has been found that $BH_3{\cdot}Me_2S$ reduces stereoselectively 2-propionyl-3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene **1** to the corresponding alcohol **2**. The configuration $(S,S_P)/(R,R_P)$ of **2** has been determined by X-ray diffraction study of the bis-$W(CO)_5$ complex (**3**) of **2**. The stereochemical outcome of this reaction has been explained assuming an *exo*-attack of borane at the *s-trans* conformation of **1**. X-Ray diffraction study and DFT calculations confirmed greater thermodynamic stability of this conformation.

Introduction

Nucleophilic addition to the carbonyl group in planar chiral organometallic aldehydes or ketones constitutes a promising route to organometallic complexes having both planar and central chirality elements, which may be of interest *e.g.* as ligands for asymmetric catalysis. Its stereochemistry has been thoroughly studied in the case of aldehydes bearing (η^6- arene)$Cr(CO)_3$,[1] (η^5-cyclohexadienyl)$Mn(CO)_3$,[2] (η^4- diene)-$Fe(CO)_3$,[3] ferrocenyl,[4] phosphaferrocenyl,[5] and 1,1′-diphosphaferrocenyl[6] moieties. In this reaction, when the nucleophile $Nu^- \neq H^-$, a stereogenic center at the formyl carbon atom is created. The stereochemical outcome of the addition is usually explained assuming that the nucleophile attacks the energetically favorable conformation of the aldehyde from the unhindered (opposite to the metal) *exo* site.

In contrast, significantly less is known about nucleophilic addition to the carbonyl group in organometallic planar chiral ketones. As far as the 1,1′-diphosphaferrocene system is concerned, Mathey *et al.*[7] found that reduction of 2-acetyl-3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene with sodium borohydride led to a ~2 : 1 mixture of diastereomeric alcohols but they have not determined the absolute configuration of the major product. Similarly, Roberts *et al.*[8] reported that reduction of 2-acetyl-3,4-dimethylphosphaferrocene afforded a ~1 : 1 mixture of diastereomeric alcohols. Assuming that nucleophile invariably attacks the metallocenyl ketone from the *exo* site this would suggest the presence of two reactive conformations for these ketones. Obviously, such non-stereoselective reactions are of limited value for synthetic purposes.

In the course of our ongoing study on chiral 1,1′-diphosphaferrocenes combining planar and central chirality elements we have become interested in elaboration of stereocontrolled methods of nucleophilic addition to 2-acyl-derivatives of 3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene. These compounds are readily available by Friedel–Crafts acylation of 3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene[7,9] and therefore are of interest as starting materials in further syntheses of derivatives of this metallocene. It is worth noting that the chemistry of 1,1′-diphosphaferrocenes continues to attract significant interest and some applications of these compounds as ligands for transition metals in homogenous catalysis have been already found.[10]

Herein, we report that a higher congener of compound studied by Mathey *et al.*,[7] 2-propionyl-3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene **1**, is reduced stereoselectively, by $BH_3{\cdot}Me_2S$ (BMS) to the corresponding alcohol, which has the same configuration as compound obtained *via* addition of EtMgBr to 2-formyl-3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene.[6b] The conformational preference for the propionyl group in **1** was determined by an X-ray diffraction study and by DFT calculations. The configuration of the alcohol, determined by X-ray diffraction is in line with the *exo*-attack of the nucleophile on the more stable *s-trans* conformation of **1**.

Results and discussion

The starting ketone **1** (racemic mixture) was prepared in 93% yield by the Friedel–Crafts acylation of 3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene with propionic acid in the presence of trifluoroacetic anhydride (TFAA) and trifluoromethanesulfonic acid (TfOH) (Scheme 1), using methodology developed in our laboratory.[9]

The X-ray diffraction analysis showed that compound **1** in the solid state adopts a conformation in which the carbonyl oxygen is situated *trans* with respect to P1 (*s-trans* conformation) (Fig. 1). Selected structural data are given in Table 1.

Theoretical calculations performed by DFT at the B3LYP/6-31G* level confirmed greater thermodynamic stability of the *s-trans* conformation of **1** in comparison to its *s-cis*

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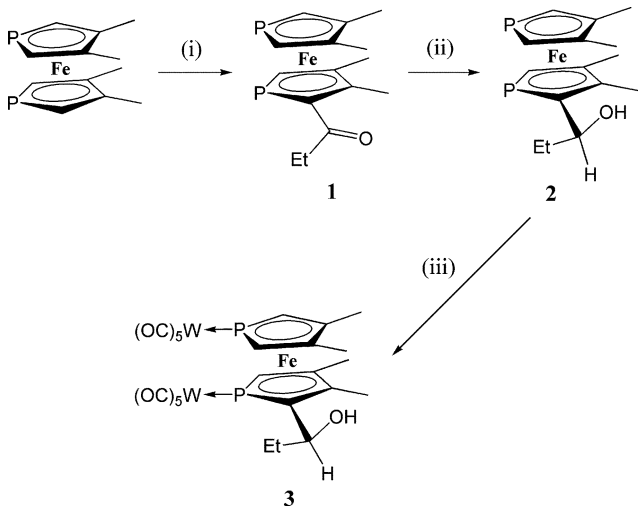

Scheme 1 *Reagents and conditions*: (i) EtCOOH–TFAA–TfOH, (ii) BMS, (iii) excess $W(CO)_5$(THF).

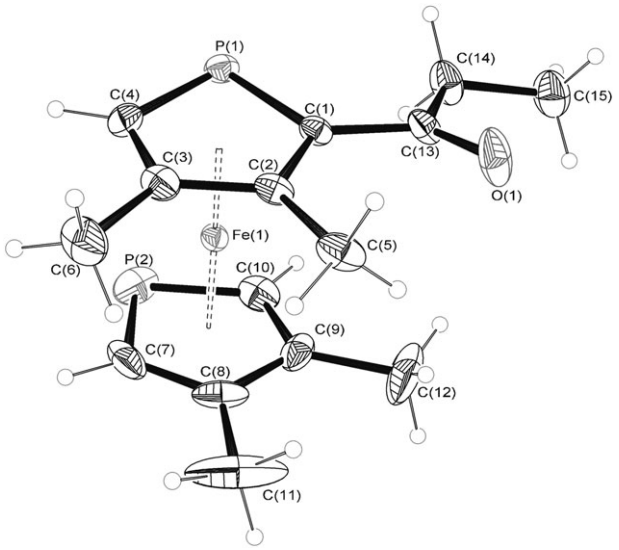

Fig. 1 Molecular structure of **1** with atom labeling scheme. The ellipsoids are presented at 50% probability level.

Table 1 Comparison of selected experimental (X-ray) and calculated (DFT) structural data for **1** and **3**

	1 (X-ray)	**1** (DFT)	**3** (X-ray)	**3** (DFT)
Fe(1)–C(1)	2.0711(14)	2.0802	2.0955(11)	2.1123
Fe(1)–C(2)	2.0829(15)	2.0856	2.0725(12)	2.0799
Fe(1)–C(3)	2.0781(17)	2.0810	2.0709(17)	2.0729
Fe(1)–C(4)	2.0795(17)	2.0863	2.0862(14)	2.0958
Fe(1)–C(7)	2.0732(18)	2.0851	2.0926(12)	2.0944
Fe(1)–C(8)	2.0913(17)	2.0862	2.0660(17)	2.0945
Fe(1)–C(9)	2.0753(18)	2.0749	2.0730(14)	2.0865
Fe(1)–C(10)	2.0689(18)	2.0715	2.0901(12)	2.0886
Fe(1)–P(1)	2.2794(5)	2.3295	2.2574(18)	2.3068
Fe(1)–P(2)	2.2848(5)	2.3273	2.2578(15)	2.3068
O(1)–C(13)	1.216(2)	1.2265	1.417(8)	1.4260
C(1)–C(13)	1.472(2)	1.4918	1.509(7)	1.5092
P(1)–C(1)–C(13)–O(1)	168.60(16)	159.12	21.1(6)	28.16

counterpart (Fig. 2). The energy difference between these conformations (4.0 kcal mol^{-1}) presumably results (at least in part) from the steric repulsion between the ethyl group of the propionyl substituent and the methyl group at C3 in the *s-cis* conformation, bringing about a twist of the CO group out of the phospholyl ligand plane (toward Fe) and weakening π-conjugation. Indeed, the values of the P1-C1-C13-O1 angle are −48 and −159° in *s-cis* and *s-trans* conformations, respectively. With the calculated energy difference the *s-cis* conformer should not be significantly populated at ambient temperatures. The calculated energy barrier for the *s-trans* to *s-cis* conversion is equal to 10 kcal mol^{-1} and the geometry of the transition state (TS) is shown in Fig. 2.

Selected calculated structural data for (*s-trans*)-**1** are included in Table 1.

It is also worth noting that in the calculated structure of (*s-trans*)**1** the carbonyl oxygen is inclined toward the iron atom, whereas in the X-ray structure (Fig. 1) it is inclined in the opposite direction. Inspection of the crystal packing of **1** (Fig. 3) provides an explanation of this phenomenon. In fact, short (2.423(3) Å) O1···H5C intermolecular contacts are present in crystals of **1**, which may be responsible for the observed O1-oxygen positioning and thermal displacement ellipsoid elongation. Molecules connected by this contact form a chain along (101) direction.

We have found that reaction of **1** with $NaBH_4$ is sluggish and accompanied by extensive decomposition processes (presumably due to the basic medium because it is known that 1,1′-diphosphaferrocenes may decompose in such media).[7] However, unexpectedly, we have discovered that **1** can be readily reduced to the diastereomerically pure alcohol **2**, isolated in 83% yield, by excess of BMS in refluxing THF. This result is surprising because it has been earlier reported that BMS reduces ferrocenyl ketones (*e.g.* propionylferrocene) to the corresponding alkylferrocenes.[11] In a recently published paper[12] it has been suggested that this unusual reduction of ferrocenyl ketones is due to the facile formation of α-ferrocenylalkyl carbenium ions. This hypothesis could explain why in the case of **1** the reduction stops at the alcohol step, because it is known that 1,1′-diphosphaferrocenyl moiety does not stabilize an adjacent carbenium ion center as well as the ferrocenyl moiety does.[5,8]

The alcohol **2** was isolated as an orange solid by silica gel column chromatography and its structure was confirmed by spectroscopic data and elemental analysis. The data obtained were the same as those displayed by the product of the reaction of 3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene-2-carbaldehyde (**4**) with EtMgBr,[6b] indicating that in both reactions the same product is formed. However, the spectra do not provide a direct information about the stereochemistry of the newly created sp^3 stereogenic center. For determination of stereochemistry of **2** we needed an X-ray diffraction analysis of this compound. Unfortunately, we were unable to obtain X-ray quality crystals of **2**. To overcome this problem we transformed **2** into its bis-$W(CO)_5$-complex (**3**) by reaction with excess of photochemically generated $W(CO)_5$(THF). The evidence for coordination of both P atoms to the $W(CO)_5$ moieties was provided by ^{31}P NMR spectrum of this compound, consisting of two singlets, each of them showing ^{183}W satellite bands with $^1J_{WP}$ ~260 Hz. Similarly as other

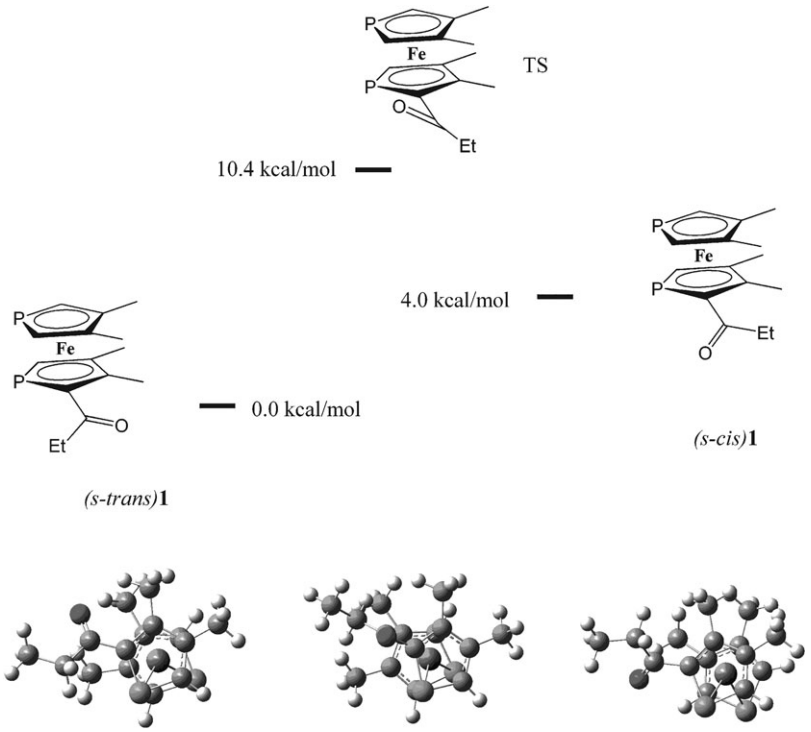

Fig. 2 Relative energies and optimized geometries of *s-cis* and *s-trans* conformations of **1** and those of the transition state for their interconversion (TS).

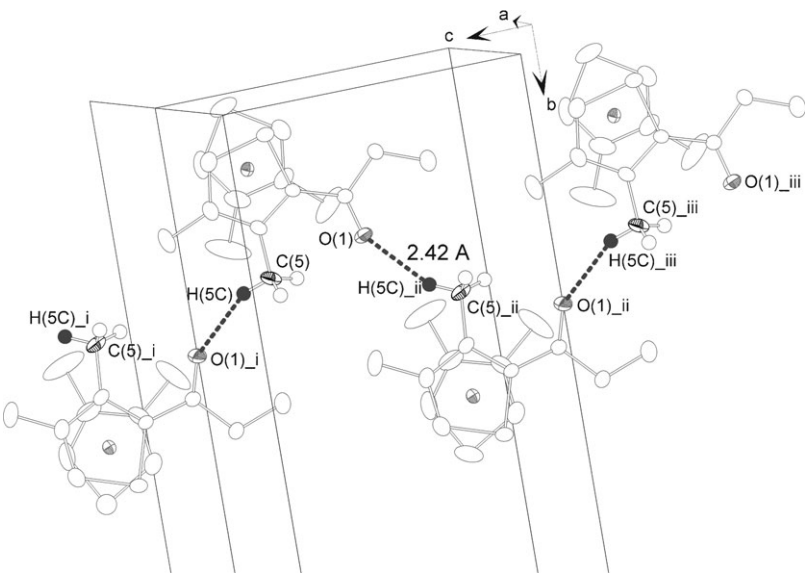

Fig. 3 Intermolecular interactions form chains of **1** molecules of **1** along the (101) crystallographic direction. Symmetry equivalents are denoted: (i) $1/2 + x, 1/2 - y, 1/2 + z$; (ii) $-1/2 + x, 1/2 - y, -1/2 + z$; (iii) $-1 + x, y, -1 + z$.

$W(CO)_5$-derivatives of 3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene,[6b,13] compound **3** readily formed crystals suitable for X-ray diffraction studies. Its molecular structure is shown in Fig. 4. DFT calculations were also carried out for this compound and selected calculated and experimental structural parameters are gathered in Table 1.

The structure reveals the $(S,S_P)/(R,R_P)$ configuration of the **2** moiety coordinated to two $W(CO)_5$ centers (in fact this structure is closely similar to that of the phenyl-substituted analog of **3**[6b]). The high level of stereocontrol observed in the reduction of **1** is in line with the presence of a single reactive conformation (*s-trans*) and the *exo*-attack of the reducing agent. Analogously, an *exo* attack of EtMgBr on the *s-cis* conformation of aldehyde **4** would also lead to **2** (Fig. 5).

Compared with the above results, low or negligible level of stereocontrol observed in the reduction of 2-acetyl-3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene[7] and 2-acetyl-3,4,-dimethylphosphaferrocene[8] suggests that for these compounds two reactive conformations are present in solution. This may be attributed to a smaller difference in effective size of the carbonyl oxygen and the methyl group, insufficient to destabilize the *s-cis* conformation.

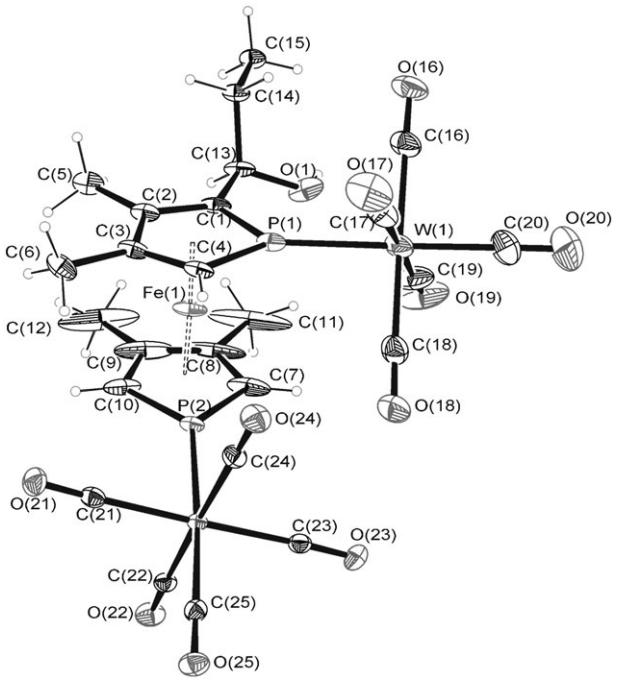

Fig. 4 Molecular structure of **3** with atom labeling scheme. The ellipsoids are presented at 50% probability level.

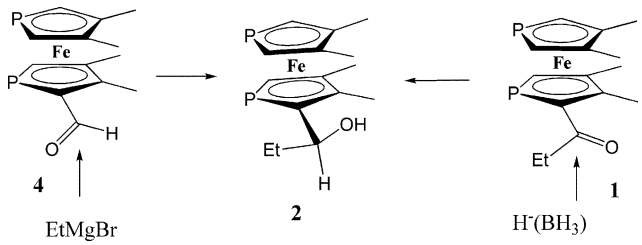

Fig. 5 Comparison of the stereochemical outcome of the nucleophilic addition to **1** and **4**.

On the other hand, it may be expected that nucleophilic addition to derivatives of **2**, bearing bulkier acyl groups will proceed with high level of stereocontrol, leading to products with predictable stereochemistry.

Conclusion

We have demonstrated that stereocontrol of the nucleophilic addition to the carbonyl group in a η^5-(2-acyl-3,4-dimethylphospholyl) ligand can be achieved when the difference in the effective sizes of the carbonyl oxygen and the alkyl part of the acyl group is sufficient for destabilization of the *s-cis* conformation of the complex. 3,4-Dimethyl-substituted phospholyl ligands are readily available and frequently used in synthesis of transition metal phospholyl complexes. Therefore, we expect that the described finding will open a stereocontrolled route to phospholyl complexes having planar and central chirality elements.

Experimental

All reactions were carried out under argon. All reagents used in this work are commercially available (Aldrich) and were used without further purifications. Compound **1** was prepared according to the literature procedure.[14] Dichloromethane was distilled over calcium hydride and THF over sodium-benzophenone before use. Chromatographic separations were carried out using Silica gel 60 (Merck, 230-400 mesh ASTM). The NMR spectra were run on a Varian Gemini 200 BB (200 MHz for ^{1}H) and IR spectra on a FT-IR Nexus spectrometer. Elemental analyses were performed by Analytical Services of the Center of Molecular and Macromolecular Studies of the Polish Academy of the Sciences (Łódź).

Synthesis

2-Propionyl-3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene (1). A mixture of propionic acid (74 mg, 75 µl, 1 mmol) and trifluoroacetic anhydride (210 mg, 140 µl, 1 mmol) was stirred for 5 min at room temperature. To this mixture a solution of 3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene (278 mg, 1 mmol) in dichloromethane (5 ml) and triflic acid (3.44 g, 2 ml, ~23 mmol) was added, the mixture was stirred for 2 h at room temperature and poured onto water. Extraction with dichloromethane, drying (Na_2SO_4), evaporation to dryness, column chromatography (eluent dichloromethane) and crystallization (dichloromethane–pentane) afforded **1** as red crystals. Yield 312 mg (93%): ^{1}H NMR ($CDCl_3$) δ 4.00 (d, $^2J_{PH}$ = 37.5 Hz, 1H, CHP), 3.67 (d, $^2J_{PH}$ = 36.0 Hz, 2H, CHP), 2.61 (m, 2H, CH_2), 2.39 (s, 3H, Me), 2.10 (s, 3H, Me), 2.04 (s, 3H, Me), 1.98 (s, 3H, Me), 1.06 (t. $^3J_{HH}$ = 7.2 Hz, 3H, CH_3 propionyl); ^{31}P NMR ($CDCl_3$) δ −53.8 (d, $^2J_{PP}$ = 12.2 Hz), −69.2 (d, $^2J_{PP}$ = 12.2 Hz). IR (KBr) 1659 cm^{-1}. Anal. Calc. for $C_{15}H_{20}FeOP_2$: C, 53.92; H, 6.03. Found: C, 53.90; H, 5.99%.

1-(3,3′,4,4′-Tetramethyl-1,1′-diphosphaferrocene-2-yl)propan-1-ol (2). A solution of **1** (290 mg. 0.86 mmol) and $BH_3{\cdot}SMe_2$ (1 ml of 2 M solution in THF, 2 mmol) in THF (10 ml) was refluxed for 2 h. After cooling to room temperature MeOH (5 ml) was added and the solvents were evaporated. Column chromatography (eluent dichloromethane–hexanes 2 : 1) and crystallization (dichloromethane–pentane) afforded **2** as orange–red crystals. Yield 240 mg (83%). ^{1}H NMR ($CDCl_3$) δ 4.19 (d, $^2J_{PH}$ = 35.8 Hz, 1H, CHP), 4.17 (m, 1H, C*H*OH), 3.54 (d, $^2J_{PH}$ = 36.2 Hz, 2H, CHP), 3.44 (d, $^2J_{PH}$ = 36.6 Hz, 1H, CHP), 2.47 (d, $^3J_{HH}$ = 4.5 Hz, OH), 2.11 (s, 3H, Me), 2.10 (s, 3H, Me), 2.07 (s, 3H, Me), 2.02 (s, 3H, Me), 1.56 (m, 2H, CH_2CH_3) 0.94 (t. $^3J_{HH}$ = 7.2 Hz, 3H, CH_3CH_2); ^{31}P NMR ($CDCl_3$) δ −77.5 (d, $^2J_{PP}$ = 9.8 Hz), −79.4 (d, $^2J_{PP}$ = 9.8 Hz). IR (KBr) 3486 cm^{-1}. Anal. Calc. for $C_{15}H_{22}FeOP_2$: C, 53.60; H, 6.60. Found: C, 53.58; H, 6.52%.

Bis-W(CO)$_5$ complex (3) of 2. Complex $W(CO)_5$(THF) was prepared by irradiation of $W(CO)_6$ (352 mg, 1 mmol) in THF (40 ml) with a 150 W mercury lamp for 2 h. To this solution complex **2** (110 mg, 0.3 mmol) was added and the solution was stirred at room temperature for 24 h. The solvent was evaporated and the residue chromatographed (eluent dichloromethane–hexane 1 : 1) and crystallized from dichloromethane–pentane. Yield 245 mg (94%). ^{1}H NMR: ($CDCl_3$) δ 4.36 (m, 1H, C*H*OH), 3.87 (d, $^2J_{PH}$ = 30.7 Hz, phospholyl) 3.84 (d, $^2J_{PH}$ = 31.8 Hz, phospholyl), 3.68 (d, $^2J_{PH}$ = 30.9 Hz,

phospholyl), 2.21 (s, 3H, Me), 2.16 (s, 3H, Me), 2.13 (s, 3H, Me), 2.09 (s, 3H, Me), 1.63 (m, 3H, CH_2 + OH), 1.02 (t, $^3J_{HH}$ = 7.2 Hz, CH_2CH_3); ^{31}P NMR ($CDCl_3$): δ −39.32 (s, with ^{183}W satellites $^1J_{WP}$ = 262 Hz), −46.78 (s, with ^{183}W satellites $^1J_{WP}$ = 258 Hz). IR (KBr, cm^{-1}): 3433 (br), 2073 (s), 1988 (m), 1924 (vs). Anal. Calc. for $C_{25}H_{22}FeO_{11}P_2W_2$: C, 30.52; H, 2.25. Found: C, 30.91; H, 2.38%.

X-Ray diffraction measurements

A summary of crystallographic data collection and refinement parameters are collected in Table 2. The data processing was carried out with Bruker[15] APEXII software, and structure solution and refinement were accomplished with SHELXS[16] and SHELXL[17] programs. The refinements were based on F^2 for all reflections except those with negative intensities. Weighted R factors wR and all goodness-of-fit S values were based on F^2, whereas conventional R factors were based on the amplitudes, with F set to zero for negative F^2. The $F_o^2 > 2\sigma(F_o^2)$ criterion was applied only for R factor calculation and was not relevant to the choice of reflections for the refinement. Scattering factors were taken from Tables 4.2.6.8 and 6.1.1.4 of ref. 18.

In the final least-squares full-matrix refinement all non-hydrogen atoms for both structures were refined with anisotropic thermal displacement parameters. Hydrogen atoms were first located directly from the Fourier map, but then refined as riding atoms with idealized geometry. In the case of both structures the unsubstituted η^5-(3,4-dimethylphospholyl) rings display significantly elongated thermal displacement ellipsoids, indicating their high mobility.

A single molecule of compound **1** constitutes the crystallographic asymmetric unit, with all atoms located in general positions. In the case of compound **3** the asymmetric unit contains also half a molecule of dichloromethane, disordered about an inversion center. Due to the fact that occupancies of the alternative conformations were all small (25%), restraints were applied on the shape of the thermal ellipsoids of the disordered atoms, in order to keep the ellipsoids close to isotropic.

DFT calculations

Theoretical calculations were performed with Gaussian 03W version E.01.[19] Structures were fully optimized at the density functional theory level employing B3LYP functional and pseudopotential LANL2DZ for W and 6-31G* basis set for all remaining atoms.

Table 2 Summary of crystallographic data and structure refinement details

	1	**3**
Crystal data		
Formula	$C_{15}H_{20}FeOP_2$	$C_{25.5}H_{22}ClFeO_{11}P_2W_2$
M_r	334.10	1025.37
Crystal size/mm	0.25 × 0.20 × 0.14	0.178 × 0.10 × 0.097
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a/Å	7.26050(10)	7.3557(6)
b/Å	22.7352(5)	21.277(2)
c/Å	9.2648(2)	20.5269(16)
β/°	99.3960(10)	98.503(5)
V/Å^3	1508.81(5)	3177.3(5)
Z	4	4
D_c/g cm^{-3}	1.471	2.144
Data collection		
Diffractometer	Bruker Kappa APEXII Ultra	Bruker Kappa APEXII Ultra
Radiation type (λ/Å)	Mo-Kα (0.71073)	Mo-Kα (0.71073)
μ/mm^{-1}	1.200	7.913
T/K	100(2)	100(2)
Limiting indices, hkl	−11 to 11, −36 to 36, −13 to 14	−10 to 10, −29 to 29, −28 to 24
Reflections collected	44533	51563
Reflections unique	6437	9276
R_{int}	0.0398	0.0372
Completeness to θ <30.0° (%)	99.1	100.0
Solution and refinement		
Solution	Direct method	Direct method
Data	6437	9276
Restraints	0	24
Parameters	177	412
Goodness-of-fit on F^2	1.067	1.083
$R(F)$ [$I > 2\sigma(I)$]	0.0431	0.0397
$wR(F^2)$ [$I > 2\sigma(I)$]	0.1028	0.0879
$R(F)$	0.0515	0.0452
$wR(F^2)$	0.1064	0.0908
Diff. peak/hole/e Å^{-3}	1.648/−1.212	5.682/−5.523

Acknowledgements

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References

1 (*a*) S. Pache, P. Romanens and E. P. Kündig, *Organometallics*, 2003, **22**, 377; (*b*) S. G. Davies and C. L. Goodfellow, *J. Chem. Soc., Perkin Trans. 1*, 1990, 393; (*c*) C. Mukai, W.-J. Cho, I. J. Kim, M. Kido and M. Hanaoka, *Tetrahedron*, 1991, **47**, 3007; (*d*) W. H. Moser, J. Zhang, C. S. Lecher, T. L. Frazier and M. Pink, *Org. Lett.*, 2002, **4**, 1981.
2 B. Jacques, A. Eloi, M. Chavarot-Kerlidou, F. Rose-Munch, E. Rose, H. Gérard and P. Herson, *Organometallics*, 2008, **27**, 2505.
3 W. A. Donaldson, *Curr. Org. Chem.*, 2000, **4**, 837.
4 (*a*) S. Fukuzawa, D. Tsuchiya, K. Sasamoto, K. Hirano and M. Ohtaguchi, *Eur. J. Org. Chem.*, 2000, 2877; (*b*) H. Li, H.-S. Cheng, A.-H. Seow and T.-P. Loh, *Tetrahedron Lett.*, 2007, **48**, 2209; (*c*) L. Bernardi, B. F. Bonini, M. Comes-Franchini, G. Dessole, M. Fochi and A. Ricci, *Phosphorus, Sulfur Silicon Relat. Elem.*, 2005, **180**, 1273.
5 L. Brassat, B. Ganter and C. Ganter, *Chem.–Eur. J.*, 1998, **4**, 2148.
6 (*a*) D. Plażuk, J. Zakrzewski and A. Rybarczyk-Pirek, *J. Organomet. Chem.*, 2006, **691**, 3098; (*b*) B. Mucha, A. Kłys, A. Rybarczyk-Pirek and J. Zakrzewski, *Tetrahedron: Asymmetry*, 2007, **18**, 1766.
7 B. De Luzon, B. Deschamps, J. Fischer, F. Mathey and A. Mitschler, *J. Am. Chem. Soc.*, 1980, **102**, 994.
8 R. M. G. Roberts, J. Silver and A. S. Wells, *Inorg. Chim. Acta*, 1989, **155**, 197.
9 D. Plażuk and J. Zakrzewski, *Synth. Commun.*, 2004, **34**, 99.
10 (*a*) A. Kłys, A. Rybarczyk-Pirek and J. Zakrzewski, *J. Organomet. Chem.*, 2008, **693**, 1166; (*b*) B. Deschamps, F. Mathey, J. Fischer and J. H. Nelson, *Inorg. Chem.*, 1984, **23**, 3455; (*c*) X. Sava, L. Ricard, F. Mathey and P. Le Floch, *Chem.–Eur. J.*, 2001, **7**, 3159; (*d*) X. Sava, M. Melaimi, N. Mézailles, L. Ricard, F. Mathey and P. Le Floch, *New J. Chem.*, 2002, **26**, 1378; (*e*) X. Sava, M. Melaimi, L. Ricard, F. Mathey and P. Le Floch, *New J. Chem.*, 2003, **27**, 1233; (*f*) M. Melaimi, L. Ricard, F. Mathey and P. Le Floch, *J. Organomet. Chem.*, 2003, **684**, 189; (*g*) P. Le Floch, *Coord. Chem. Rev.*, 2006, **205**, 627.
11 (*a*) D.-H. Kim, E.-S. Ryu, C. S. Cho, S. C. Shim, H.-S. Kim and T.-J. Kim, *Organometallics*, 2000, **19**, 5784; (*b*) L. Routaboul, J. Chiffre, G. G. A. Balavoine, J.-C. Daran and E. Manoury, *J. Organomet. Chem.*, 2001, **637–639**, 364.
12 R. Šebesta, M. Meciarová, E. Molnár, J. Csimadiová, P. Fodran, O. Onomura and Š. Toma, *J. Organomet. Chem.*, 2008, **693**, 3131.
13 A. Kłys, M. Małecka and J. Zakrzewski, *Arkivoc*, 2007, 172.
14 F. Mathey and G. de Lauzon, *Organomet. Synth.*, 1986, 251.
15 BRUKER-Nonius AXS, 2007.
16 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.
17 G. M. Sheldrick, SHELXL93. *Program for the Refinement of Crystal Structures*, University of Göttingen, Germany.
18 *International Tables for Crystallography*, ed. A. J. C. Wilson, Kluwer, Dordrecht, 1992, vol. C.
19 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *Gaussian 03 (Revision E.01)*, Gaussian Inc., Wallingford, CT, 2004.

