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Synthesis and characterisation of palladium(II) complexes with hybrid phosphinoferrocene ligands bearing additional O-donor substituents[†]

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While 1,1'-bis(diphenylphosphino)ferrocene (dppf) is widely used as a ligand in coordination chemistry and catalysis, its congeners with oxygen-containing functional groups have long been overlooked. Accordingly, we studied the coordination behaviour in Pd(II) complexes of three phosphinoferrocene ligands bearing secondary O-donor groups, Ph₂PfcR, wherein R = CHO (**1**), Ac (**2**) and CMe₂(OH) (**3**), and fc = ferrocene-1,1'-diyl. Depending on the stoichiometry, reactions of **1-3** (L) with [PdCl₂(cod)] (cod = $\eta^2:\eta^2$ -cycloocta-1,5-diene) produced the respective mono- and dipalladium complexes, *trans*-[PdCl₂(L- κP)₂] and *trans*-[PdCl(μ -Cl)(L- κP)]₂. Compound [PdCl(μ -Cl)(**3**- κP)]₂ was found to dehydrate readily, giving rise to [PdCl(μ -Cl)(Ph₂PfcC(Me)=CH₂- κP]₂. Furthermore, ligands **1-3** cleaved [(L^{NC})Pd(μ -Cl)]₂ (L^{NC} = **2**-((dimethylamino- κ N)methyl)phenyl- κC^1 , yielding [(L^{NC})PdCl(L- κP)], which were converted into the cationic complexes [(L^{NC})PdCl(L)]X (L/X = **1**/PF₆, **2**/SbF₆, **3**/PF₆). Compounds with ligands **1** and **2** were structurally authenticated as stable bis-chelate complexes. In contrast, the product featuring ligand **3** was rather unstable and converted into [(L^{NC})PdCl(L)]X (μ -Cl₃)[PF₆] upon recrystallisation. Weak oxygen coordination was confirmed via reactions of [(L^{NC})PdCl(L)]X with (PhCH₂NEt₃)Cl in which the parent chloride complexes were regenerated, and was further corroborated by DFT computations. Our findings, pointing to hemilabile coordination of **1-3**, are relevant for catalysis because de-coordination of the weaker binding O-donor moiety may open a vacant site for a substrate, thereby enhancing the catalytic properties of metal complexes with ligands of this type.

Introduction

Replacing one phosphine substituent in the extensively studied 1,1'-bis(diphenylphosphino)ferrocene (dppf)¹ provides access to a vast family of structurally diverse functional phosphinoferrocene ligands (Scheme 1).² In this regard, compounds with chemically dissimilar donor moieties are particularly relevant as hybrid ligands capable of hemilabile coordination.³ In addition, such compounds can serve as advanced synthetic building blocks. Among dppf analogues bearing oxygen functions, research efforts have focused on 1'-(diphenylphosphino)ferrocene-1-carboxylic acid (Hdpf),⁴ which has been studied as a ligand in coordination compounds⁵ and converted into new ligands, primarily phosphinoferrocene amides⁶ and oxazolines.⁷ In contrast, compounds containing chemically related aldehyde (CHO) and alcohol (CH₂OH) groups have been studied considerably less than Hdpf.⁸ For instance, aldehyde $\mathbf{1}^{9,10,11}$ (Scheme 1) has been used to synthesize phosphinoferrocene ligands,^{9,12} but its coordination properties

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remain unexplored. A similar situation is encountered for 1'-(diphenylphosphino)-1-(hydroxymethyl)ferrocene $(3^*)^{11,13}$ and 1'-(diphenylphosphino)-1-acetylferrocene (2; Scheme 1).^{14,15}



Considering this knowledge gap, we aimed to investigate the coordination behaviour of these archetypal hybrid O,P-ligands, specifically in Pd(II) complexes¹⁶ with simple terminal (i.e., halide) and N,C-chelating auxiliary ligands. For such purpose, we chose structurally related compounds, namely the aforementioned aldehyde **1**, acyl derivative **2**, and an alcohol bearing 2-hydroxyprop-2-yl substituent, compound **3** (Scheme 1). Hence, in this contribution, we report the synthesis and detailed structural characterisation by spectroscopic, X-ray diffraction and DFT computational methods of Pd(II) complexes accommodating these compounds as ligands.

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⁺ Electronic Supplementary Information (ESI) available: complete experimental details including those on structure determination and on DFT computations, additional structural diagrams, copies of the NMR spectra (PDF), and Cartesian coordinates of the DFT optimized structures (MOL2). CCDC 1882120-1882129. See DOI: 10.1039/x0xx00000x

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Results and discussion

Aldehyde **1** was synthesized as previously reported.¹¹ However, attempts to prepare **2** using a modified literature method (Scheme 2), i.e., from acetyl chloride and 1'-(diphenylphosphino)-1-lithoferrocene generated *in situ* from bromide **4** and *n*-butyllithium,^{2a,10} instead of opening 1-phenyl-1-phospha[1]ferrocenophane with phenyllithium, as originally reported,¹⁴ reproducibly led to disappointingly low yields (12%). Whilst searching for an alternative synthesis, we found that the yield of **2** increases when replacing acetyl chloride with the corresponding Weinreb amide.¹⁷ Thus, lithiation of **4** followed by *N*-methoxy-*N*-methylacetamide addition gave rise to **2** in 55% yield after simple chromatographic purification.





Alcohol **3**, completing the series of ligands, was similarly synthesized by lithiation of bromide **4** and by quenching of the intermediate organolithium with dry acetone (42% yield). Similarly to **2**, compound **3** was isolated along with (diphenylphosphino)ferrocene (FcPPh₂, Fc = ferrocenyl), which results from unwanted protonolysis of the lithiated intermediate.



In their ¹H and ¹³C NMR spectra, compounds 2 and 3 displayed characteristic sets of signals attributed to the 1,1'disubstituted ferrocene unit. Resonances of the polar substituents were observed at δ_{H} 2.31, δ_{C} 27.49 (COMe) and δ_{C} 201.94 (COMe) for **2**, and at δ_{H} 1.43, δ_{C} 31.05 (CMe₂) and δ_{C} 68.91 (CMe₂) for 3. The presence of the phosphine moiety was shown by the ¹H and ¹³C (³¹P-coupled¹⁸) NMR signals of the PPh₂ group and by the ³¹P NMR resonances at $\delta_P \approx -17$. The IR spectra of **2** and **3** showed a strong $v_{c=0}$ band at 1663 cm⁻¹ (cf. 1662/1655 cm⁻¹ for acetylferrocene¹⁹) and a broad band due to v_{OH} vibration at 3447 cm⁻¹ with a weaker absorption at 3568 cm⁻¹, respectively. Differences in the extent of conjugation, highlighted already by the colour of the compounds (1 and 2 are burgundy red, 3 is orange brown), corresponded to the positions of the low-energy bands in their UV-vis spectra (Figure 1). Specifically, a weak ligand-field band at 440 nm in the spectrum of the unsubstituted ferrocene²⁰ was shifted to 459 and 454 nm for 1 and 2, respectively, but remained virtually unaffected in the spectrum of 3 (≈443 nm).



The crystal structure of **2** was determined by X-ray diffraction analysis (Figure 2). The cyclopentadienyl rings in the molecule of **2** are tilted by 1.37(9)° and adopt an intermediate conformation which brings the substituents into the *anti*position ($\tau = -165.9(1)$ °; τ is the torsion angle C1-Cg1-Cg2-C6, wherein Cg1 and Cg2 are the centroids of the cyclopentadienyl rings C(1-5) and C(6-10), respectively, and C1 and C6 are the pivotal atoms of the cyclopentadienyl rings). The C11=O bond (1.220(2) Å) in **2** has a length identical to that in acetylferrocene (1.222 Å)²¹ and lies in the plane of its parent cyclopentadienyl ring (twist angle: 5.5(1)°). The P-C bond lengths (P-C6 1.809(1) Å, and P-C12/C18 1.835(1) Å) compare very well with those determined for FcPPh₂.²²





Synthesis and characterisation of Pd(II) complexes with chloride supporting ligands. Mixing compounds 1-3 with [PdCl₂(cod)] (cod = cycloocta-1,5-diene) at a 2:1 ligand-tometal ratio led to bis(phosphine) complexes 5 (Scheme 4). When the amount of ligand was reduced to one molar equivalent, the reaction exclusively produced chloride-bridged dipalladium(II) complexes 6. In both cases, the ferrocene ligands coordinated in *trans* positions and as P-monodentate donors. Such coordination is in accordance with the low propensity of the Pd(II) ions to coordinate hard oxygen

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donors.¹⁶ Thus, although the oxygen atoms in the functional substituents are properly positioned to form O,P-chelate rings (see below), the Pd(II) ions preferably share the relatively softer chloride ligands, forming dimers 6.



Complexes 6 crystallise less readily than their monopalladium counterparts 5, and the extended times required for their crystallisation may allow decomposition. For instance, the attempted crystallisation of 6c produced mixtures of this compound and a new complex **6d**, resulting from dehydration. Compound 6c can be prepared in non-halogenated solvents (e.g., benzene, ethyl acetate or acetone) or in their HCl-free halogenated alternatives. However, when using halogenated solvents, the product must be isolated rapidly to avoid dehydration promoted by traces of HCl. This observation was corroborated by an independent experiment in which a tiny drop of methanolic HCl was added to in situ generated 6c, causing a clean and rapid conversion of this complex into 6d (within 30 min). Notably, complex 5c did not dehydrate upon recrystallisation and reacted only sluggishly with HCl.

Complexes 5 and 6 exhibited similar sets of signals due to the phosphinoferrocene ligands in their ¹H NMR spectra but could be clearly distinguished by their ³¹P NMR shifts (5: $\delta_P \approx 15$; 6: $\delta_P \approx$ 30-32).²³ In addition, the ¹³C{¹H} NMR spectra of the bis(phosphine) complexes 5 displayed signals of ³¹P-coupled carbon atoms as apparent triplets arising from virtual coupling in the AXX' spin systems of the type ${}^{13}C(A)-{}^{31}P(X)-Pd-{}^{31}P(X')-$ ¹²C, which is not observed in complexes **6**.²⁴

46 All bis(phosphine) complexes, 5a·2CH₂Cl₂, 5b and 5c, were structurally characterised by X-ray diffraction analysis. Their 48 molecular structures are shown in Figure 3 and the selected geometric parameters are outlined in Table 1. Compounds 50 5a·2CH₂Cl₂ and 5b crystallise with the symmetry of the triclinic space group P-1 and with the complex molecules lying over 52 the inversion centres. Conversely, compound 5c crystallises in the space group C2/c with the two-fold axis perpendicular to 54 the coordination plane and passing through the Pd atom.

55 The Pd-donor distances determined for the 5-type complexes 56 are similar along the series and match the bond lengths 57 determined for complex with the non-functionalised ligand, trans-[PdCl₂(FcPPh₂)₂].²⁵ The interligand angles in **5a-c** depart 58 59 from the ideal 90° only marginally. However, while the 60

coordination planes of 5a·2CH2Cl2 and 5b are exactly planar due to the imposed symmetry, the coordination geometry an 5c is distorted towards tetahedral (Cl-Pd-Cl' = 171.71(3)°, P-Pd- $P' = 167.65(2)^\circ$). The ferrocene units in **5a**·2CH₂Cl₂ and **5b** assume approximately eclipsed anticlinal conformations,^{1a} which divert their polar substituents from the Pd atom, and the substituents are coplanar with their parent cyclopentadienyl rings to maximise conjugation. In contrast, the cyclopentadienyl rings in 5c are rotated to an intermediate conformation (cf. the τ angles in Table 1), and the nonconjugated C11-OH moieties are directed towards the chloride ligands, forming O-H…Cl hydrogen bonds (O…Cl = 3.223(2) Å). *** Figure 3 near here ***

Table 1. Selected	distances and angles	s and angles for 5a ·2CH₂Cl₂, 5b and 5c (in Å and deg). ^a				
Darameter	5a,2CHaCla	56	50			
Pd-Cl	2.2926(4)	2.2959(5)	2.2971(5)			
Pd-P	2.3396(4)	2.3420(5)	2.3308(5)			
CI-Pd-P	86.49(1) ^c	88.31(2) ^c	89.59(2)/ 89.52(2)			
∠Cp1,Cp2	4.2(1)	1.5(1)	3.7(1)			
τ	146.0(1)	147.6(2)	82.9(2)			
C11-O	1.206(3)	1.220(3)	1.430(3)			
C11-O/Cp1 ^b	5.4(2)	2.1(2)	20.2(2)			

^a Definitions: Cp1 and Cp2 are the cyclopentadienyl rings C(1-5) and C(6-10), and Cg1/Cg2 stand for their respective centroids. τ = torsion angle C1-Cg1-Cg2-C6. Angle at which the C11-O bond intersects the Cp1 plane. ^c The adjacent interligand angles sum up to 180° for symmetry reasons.

Of the dimeric complexes 6, only 6a·2CHCl₃, 6b·CHCl₃ and 6d provided crystals suitable for X-ray diffraction analysis (Figure 3, Table 2). Although similar in the geometry around individual Pd centres, the compounds differed in the arrangement of their dipalladium cores. While the entire $\{Pd(\mu-CI)CIP\}_2$ moieties in 6a·2CHCl₃ and 6d are planar, owing to imposed inversion symmetry, in 6b·CHCl₃, the {PdCl₃P} planes are tilted by 41.93(3)° into a butterfly arrangement, similar to $[Pd(\mu -$ Cl)Cl(Ph₂PfcPO₃Et₂- κ P)]₂·H₂O²³ (tilt angle: 40.91(5)°; fc = ferrocene-1,1'-diyl). Although such a tilting is not unprecedented, the majority (≈75%) of structurally characterised $[Pd(\mu-Cl)Cl(PR_3-\kappa P)]_2$ complexes (PR₃ is a nonchelating phosphine) are planar or nearly planar (tilt angles <2°).²⁶ A moderate twisting may indeed occur when steric effects come into play,²⁷ but a tilting as high as by 75° could be enforced via $\pi \cdots \pi$ interactions of aromatic substituents.²⁸

The geometric parameters of 6a·2CHCl₃, 6b·CHCl₃ and 6d are generally similar to the parameters determined for [Pd(µ-Cl)Cl(Ph₂PfcPO₃Et₂- κP)]₂. In particular, the Pd-Cl(terminal) bonds in 6 are shorter than those involving the bridging chloride ligand, and the Pd-Cl(bridge) bonds with the phosphine moiety in the trans position are elongated (approximately by 0.1 Å) compared to the Pd-Cl(bridge) bonds located trans to the other chloride ligand, reflecting the stronger trans influence of the phosphine donors.²⁹ Trans influence also affects the Pd-P bonds in **6**, which are ≈ 0.1 Å shorter than those in complexes 5.

The ferrocene units in 6a·2CHCl₃, 6b·CHCl₃ and 6d exert a larger tilting (up to 7°) than those in 5. In 6a.2CHCl₃, the ferrocene substituents are located in roughly anti positions,

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and the C11=O bonds remain in the planes of their bonding cyclopentadienyl rings. Conversely, in **6b**·CHCl₃ and **6d**, the ferrocene substituents are rotated closer, and the C=O or C=C bonds are twisted by 10-20°.³⁰

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able 2. Selecte	d distances and a	angles for 6a ·2CHC	Cl ₃ , 6b ·CHCl ₃ and 6	d (in Å and de
Parameter Pd-Cl _t	6a ·2CHCl₃ 2.2740(5)	6b·CHCl₃		6d
		2.2847(9) ^c	2.2795(9)	2.2841(9)
	(Cl1)	(Pd1)	(Cl4) ^d	(Cl1)
$Pd\text{-}Cl_{b}$	2.3199(5)	2.4391(8) ^c	2.3273(9)	2.329(1)
	(Cl2)	(Cl2)	(Cl2) ^d	(Cl2)
$Pd\text{-}Cl_{b}$	2.4317(5)	2.3077(9)	2.4091(9)	2.421(1)
	(Cl2′)	(CI3) ^c	(Cl3) ^d	(Cl2')
Pd-P	2.2224(5)	2.2268(8)	2.2354(8)	2.2292(8)
		(P1)	(P2)	
$P-Pd-Cl_t$	87.82(2)	88.17(3)	88.57(3)	90.51(3)
	(Cl1)	(P1/Cl1) ^c	(P2/Cl4) ^d	(Cl1)
$P-Pd-Cl_{b}$	96.35(2)	93.49(3)	96.93(3)	94.32(3)
	(Cl2)	(P1/Cl3) ^c	(P2/Cl2) ^d	(Cl2)
Cl_t -Pd- Cl_b	89.68(2)	93.23(3)	89.13(3)	90.48(3)
	(Cl1/2')	(Cl1/2) ^c	(Cl4/3) ^d	(Cl1/2')
Cl_b -Pd- Cl_b	86.77(2)	85.08(3)	85.34(3)	84.84(3)
	(Cl2/2')	(Cl2/3) ^c	(Cl2/3) ^d	(Cl2/2')
∠Cp1,Cp2	5.2(1)	7.0(2) (Fe1)	3.0(2) (Fe2)	5.0(2)
τ	-160.0(1)	-77.2(2)	79.1(2)	-87.6(2)
		(Fe1)	(Fe2)	
C11-0	1.213(2)	1.222(6)	1.218(5)	1.318(7) ^e
		(Fe1)	(Fe2)	
C11-O/Cp1 ^b	1.4(1)	14.2(3)	8.9(3) (Fe2)	19.6(3) ^e
	.,	(Fe1)		

^a The parameters are defined as for complexes **5** (see footnote to Table 1). Cl^t and Cl^b are terminal and bridging chloride ligands. ^b Angle at which the C11-O bond intersects the Cp1 plane. ^c Pd = Pd1. ^d Pd = Pd2. ^e Parameters involving the C11-C24 double bond rather than the C11-O bond.

Synthesis and characterisation of (L^{NC})Pd(II) complexes Subsequent experiments focused on Pd(II) complexes with a 2-[(dimethylamino- κN)methyl]phenyl- κC^1 (L^{NC}) ancillary ligand and primarily aimed to engage the oxygen donor groups in coordination (Scheme 5). The first reactions in which the dimeric precursor $[(L^{NC})Pd(\mu-CI)]_2$ was cleaved with stoichiometric amounts of ligands 1-3 afforded complexes 7a-c in quantitative yields. However, the subsequent removal of Pdbound chloride ligands expected to provide cationic O,Pchelate species proved less straightforward. While the reaction between **7b** and Ag[SbF₆] produced chelate complex **8b**, similar reactions with 7a and 7c resulted in oxidation (presumably of the ferrocene ligands) and decomposition. Replacing Ag[SbF₆] with TI[PF₆] circumvented this problem and made it possible to isolate stable complexes 8a and 8c. Compounds 8a and 8b could be crystallised and were thus structurally authenticated by X-ray diffraction. The formulation of 8c was only based on spectroscopic data and on elemental analysis. Repeated attempts to crystallise 8c failed, except when using ethyl acetate/hexane, thereby producing a few crystals of $[(L^{NC})Pd(AcOEt-\kappa O)(\mathbf{3}-\kappa P)][PF_6]$ (9).

Notably, compounds **8a-c** could be transformed back to their precursors **7a-c** by adding a chloride source (Scheme 5), which

in turn suggests that the oxygen donor moieties are relatively weakly coordinated. DOI: 10.1039/C9NJ00298G



Scheme 5. Synthesis of (L^{NC})Pd(II) complexes 7 and their transformations

According to the NMR spectra, complexes **7-8** are exclusively formed as *trans*-P,N isomers, wherein the ligands with the strongest *trans* influence occupy *cis* positions.³¹ This was indicated by the splitting of the ¹H and ¹³C NMR resonances due to the CH₂NMe₂ moieties into characteristic ³¹P-coupled doublets.³² The coordination of the phosphine moieties and carbonyl groups was inferred from the low-field ³¹P NMR signals (**7a-c**: δ_P 32-33, **8a/8b**: $\delta_P \approx 29$) and from the shifts of the v_{C=0} bands to lower energies (**8a**: 1600 cm⁻¹, **8b**: 1598/1582 cm⁻¹). A similar shift was observed for the v_{C=0} band of **9** (1652 cm⁻¹ vs. 1742 cm⁻¹ for AcOEt in CCl₄³³). The IR and NMR spectra further attested the presence of the counter anions. Finally, the ESI+ MS spectra of **7** and **8** displayed fragments attributable to the cations [(L^{NC})Pd(L)]⁺ (L = **1-3**).

Unfortunately, no such direct evidence was obtained for 8c. The spectra indeed showed signals due to P-coordinated **3** (δ_P 31.8) and the signature of the PF_6^- anion but were less conclusive on the role of the CMe2(OH) group. The most striking feature observed in the IR spectrum of 8c was a sharp, medium-intensity band at 3524 cm⁻¹, which replaced the broad and composite v_{OH} bands observed in the spectra of **3** and 7c. In addition, the NMR signals assigned to the CMe₂(OH) moiety shifted when converting 7c into 8c (7c/8c: $CMe_2 \delta_H$ 1.46/1.58, δ_{C} 31.61/32.16, and CMe₂ δ_{C} 68.66/72.83) and the signal due to CMe₂ in 8c was split into a doublet, indicating coordination of the alcohol function, though perhaps hemilabile as indicated by broadening of the ¹H and ¹³C NMR signals. Here, it must be noted that fully characterized Pd(II) complexes with coordinated phosphine and alcohol functions remain extremely rare. A search in the Cambridge Crystallographic Database revealed only one such compound for which a crystal structure was determined, namely a

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(L^{NC})Pd(II) complex with O,P-chelating monoterpenic phosphinoalcohol.³⁴ The crystal structures of **8a, 8b** and **9** are shown in Figure 5.

Relevant structures of **8a**, **8b** and **9** are shown in Figure 5. Relevant structural parameters are presented in Table 3. Among these compounds, **8b** crystallized as the solvate **8b**·1/4CHCl₃ with disordered solvent and with two structurally independent but practically identical formula units (Figure S10).

The palladium atoms in **8a**, **8b** and **9** have identical donor sets in terms of the donor atoms and the type of the donor moieties. Their coordination environments are twisted due to varying Pd-donor distances³⁵ and steric demands of the chelating ligands. The L^{NC} ligands expectedly form the smallest interligand angles (82-83°), while the most opened are the angles associated with the O,P-chelating ligands (97-100°) in **8a** and **8b** or, alternatively, the P-Pd-C angle in **9**, where steric crowding between the phenyl rings occurs.

Chelate coordination significantly distorts the molecules of the ferrocene ligands in **8a** and **8b**. The donor substituents are rotated towards each other albeit without notable tilting of the ferrocene scaffold (tilt angles < 3°). In addition, the pivotal C-C(O) bonds are deflected from the planes of their bonding cyclopentadienyl rings (Table 3) and the C=O bonds are rotated. No such distortion is observed at the phosphinylated cyclopentadienyl rings. In contrast, the ferrocene ligand in **9** adopts an open conformation with the substituents located in roughly *anti* positions.

*** Figure 5 near here ***

Parameter	8a	8b ·1/4CHCl ₃	8b·1/4CHCl ₃	9
		(molecule 1)	(molecule 2)	
Pd-P	2.263(1)	2.269(1)	2.266(1)	2.2745(5)
Pd-O	2.153(5)	2.175(3)	2.176(3)	2.173(1)
Pd-C	1.999(6)	2.004(4)	2.006(4)	2.005(2)
Pd-N	2.118(4)	2.135(3)	2.141(3)	2.139(2)
P-Pd-O	97.2(1)	98.19(8)	99.93(9)	92.76(4)
P-Pd-C	92.4(2)	92.0(1)	91.3(1)	95.58(6)
C-Pd-N	82.7(2)	81.9(2)	82.3(2)	82.75(7)
N-Pd-O	88.8(2)	88.1(1)	86.7(1)	88.78(6)
∠Cp1,Cp2	2.1(4)	2.6(3)	2.6(3)	4.8(1)
τ	54.8(5)	60.4(3)	60.3(3)	159.1(2)
C=O	1.233(8)	1.241(6)	1.240(5)	1.231(3) [°]
C1-C(O)/Cp1 ^b	14.6(4)	12.1(3)	9.2(3)	n.a.

^a The parameters are defined as for complexes 5 (see footnote to Table 1). ^b Angle between the pivotal C1-C11 bond and the Cp1 plane. ^{c e} C=O bond in the coordinated ethyl acetate.

DFT computations. Differences in the behaviour of the complex cations $[(L^{NC})Pd(L)]^{+}(L = 1-3)$ were further analysed by DFT theoretical calculations at the M06/def-TZVP:sdd(Fe,Pd) level of theory by modelling the reactions of the cations $[(L^{NC})Pd(L-\kappa^{2}O,P)]^{+}$ with ethyl acetate. An inspection of the Gibbs free energies (in both gas phase and chloroform) already showed that while the conversion of $[(L^{NC})Pd(3-\kappa^{2}O,P)]^{+}$ into $[(L^{NC})Pd(3-\kappa P)(AcOEt-\kappa O)]^{+}$ is slightly exergonic, similar processes involving cations $[(L^{NC})Pd(L-\kappa^{2}O,P)]^{+}$, wherein L = 1 and 2, are energetically unfavourable (Scheme 6).



Conclusion

The results reported in this paper illustrate differences in the behaviour of structurally analogous phosphinoferrocene ligands bearing oxygen functional groups. In complexes with soft Pd(II) ions, the phosphine group serves as the primary coordination site, while the weaker-binding secondary Odonor moieties differentiate the ligands. Ligands 1 and 2 bearing formyl and acetyl substituents can be easily converted from the P-monodentate into an O,P-chelating form when a vacant coordination site is generated at palladium (in the absence of better donors). These ligands give rise to smaller and, because of a limited mobility of their conjugated C(O)R substituents, also more rigid chelate rings, making the chelate complexes reasonably stable. For ligand 3, an analogous reaction affords a product whose NMR spectra indicate labile coordination of the alcohol function. However, alcohols are harder (less polarisable) donors than aldehydes and ketones and, therefore, coordinate Pd(II) less willingly. The results from DFT calculations correspond to experimental observations, indicating an easy de-coordination of the hydroxyl group.

Overall, the differences in the affinity of donor groups present in hybrid phosphine ligands³ 1-3 towards palladium(II) may result in hemilabile coordination and facilitate the cleavage of Pd-O bonds by competing donors. This was shown by the reactions of the O,P-chelate complexes 8 with a chloride source, which cleanly regenerated chloride complexes 7 and, previously, also by the reaction of $[(L^{NC})PdCl(Ph_2PfcCO_2Me-\kappa P)]$ with AgClO₄ in acetonitrile, which produced the cationic complex [(L^{NC})Pd(MeCN-κN)(Ph₂PfcCO₂Me-κP)]ClO₄ instead of any O,P-chelate.³⁶ Despite lowering the stability of the formed species, however, the presence of the weakly bonded O-donor groups can positively affect catalytic properties of the complexes. In particular, de-coordination of the weaker binding moiety can open a vacant site for the substrate and thus assist the catalytic process. Once the catalytic transformation is over and the product is released from the

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coordination sphere, the secondary donor group can bind again thereby stabilising the catalytic intermediate.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

- a) K.-S. Gan and T. S. A. Hor in *Ferrocenes: Homogeneous Catalysis, Organic Synthesis, Materials Science* (Eds.: A. Togni and T. Hayashi), VCH, 1995, ch. 1, pp. 3-104; b) S. W. Chien and T. S. A. Hor in *Ferrocenes: Ligands, Materials and Biomolecules* (Ed.: P. Štěpnička), Wiley, Chichester, 2008, ch. 2, pp. 33-116; c) G. Bandoli and A. Dolmella, *Coord. Chem. Rev.*, 2000, **209**, 161; d) D. J. Young, S. W. Chien and T. S. A. Hor, *Dalton Trans.*, 2012, **41**, 12655.
- 2 a) P. Štěpnička in Ferrocenes: Ligands, Materials and Biomolecules (Ed.: P. Štěpnička), Wiley, Chichester, 2008, ch.
 5, pp. 177-204; b) P. Štěpnička in PATAI's Chemistry of Functional Groups, volume The Chemistry of Organoiron Compounds (Eds.: I. Marek and Z. Rappoport), Wiley, Chichester, 2013; ch. 4, pp. 103-154.
- 3 a) C. S. Slone, D. A. Weinberger and C. A. Mirkin, *Progr. Inorg. Chem.*, 1999, 48, 233; b) A. Bader, E. Lindner, *Coord. Chem. Rev.*, 1991, 108, 27.
- 4 J. Podlaha, P. Štěpnička, J. Ludvík and I. Císařová, Organometallics, 1996, 15, 543.
- 5 P. Štěpnička, Eur. J. Inorg. Chem., 2005, 3787.
- 6 P. Štěpnička, Coord. Chem. Rev., 2017, **353**, 223.
- 7 a) W. Zhang, Y. Yoneda, T. Kida, Y. Nakatsuji and I. Ikeda, *Tetrahedron: Asymmetry*, 1998, 9, 3371; b) D. Drahoňovský,
 I. Císařová, P. Štěpnička, H. Dvořáková, P. Maloň and D. Dvořák, *Collect. Czech. Chem. Commun.*, 2001, 66, 588.
- 8 Another representative of this class of compounds, 1'-(diphenylphosphino)-1-hydroxyferrocene, has been studied by Long *et al.*: a) R. C. J. Atkinson, V. C. Gibson, N. J. Long, A. J. P. White and D. J. Williams, *Dalton Trans.*, 2004, 1823; b) R. C. J. Atkinson, V. C. Gibson, N. J. Long and A. J. P. White, *Dalton Trans.*, 2010, **39**, 7540.
 - 9 M. E. Wright, Organometallics, 1990, 9, 853.
 - 10 I. R. Butler and R. L. Davies, Synthesis, 1996, 1350.
 - 11 P. Štěpnička and T. Baše, Inorg. Chem. Commun., 2001, **4**, 682.
- 12 a) T. Mino, H. Segawa and M. Yamashita, J. Organomet. Chem., 2004, 689, 2833; b) P. Štěpnička and I. Císařová, Collect. Czech. Chem. Commun., 2006, 71, 215; c) A. Hildebrandt, N. Wetzold, P. Ecorchard, B. Walfort, T. Rüffer and H. Lang, Eur. J. Inorg. Chem., 2010, 3615; d) P. Štěpnička and I. Císařová, Dalton Trans., 2013, 42, 3373; e) K. Škoch, I. Císařová and P. Štěpnička, Inorg. Chem., 2014, 53, 568; f) K. Škoch, I. Císařová and P. Štěpnička, Organometallics, 2015,

View Article Online **34**, 1942; g) P. Štěpnička, M. Zábraríšký and R. Císařová *Organomet. Chem.*, 2017, **846**, 193; h) O. Bárta, I. Císařová and P. Štěpnička, *J. Organomet. Chem.*, 2018, **855**, 26.

- P. Štěpnička, I. Císařová and J. Schulz, Organometallics, 2011, 30, 4393.
- 14 I. R. Butler and W. R. Cullen, Can. J. Chem., 1983, 61, 147.
- 15 It is worth noting that compound 2 is an isomer of the "enolizable" ketophosphine FcC(O)CH₂PPh₂. Selected references: a) P. Braunstein, T. M. Gomes Carneiro, D. Matt, F. Balegroune and D. Grandjean, J. Organomet. Chem., 1989, **367**, 117; b) P. Braunstein, L. Douce, F. Balegroune, D. Grandjean, D. Bayeul, Y. Dusausoy and P. Zanello, New. J. Chem., 1992, **16**, 925; c) D. Matt, M. Huhn, J. Fischer, A. De Cian, W. Kläui, I. Tkatchenko and M. C. Bonnet, J. Chem. Soc., Dalton Trans., 1993, 1173; d) P. Braunstein, D. G. Kelly, A. Tiripicchio and F. Ugozzoli, Inorg. Chem., 1993, **32**, 4845.
- 16 a) C. F. J. Barnard and M. H. J. Russel, *Palladium* in *Comprehensive Coordination Chemistry* (Eds.: G. Wilkinson, R. D. Gillard and J. A. McCleverty), Pergamon Press: Oxford, 1987, vol. 5, pp. 1099-1130; b) A. T. Hutton and C. P. Morley, *Palladium(II): Phosphorus Donor Complexes* in *Comprehensive Coordination Chemistry* in *Comprehensive Coordination Chemistry* (Eds.: G. Wilkinson, R. D. Gillard and J. A. McCleverty), Pergamon Press: Oxford, 1987, vol. 5, pp. 1157-1170.
- 17 a) S. Nahm and S. M. Weinreb, *Tetrahedron Lett.*, 1981, 22, 3815; b) M. Mentzel and H. M. R. Hoffmann, *J. Prakt. Chem.*, 1997, 339, 517; c) S. Balasubramaniam and I. S. Aidhen, *Synthesis*, 2008, 3707.
- 18 H.-O. Kalinowski, S. Berger and S. Braun, ¹³C-NMR-Spektroskopie, Thieme, Stuttgart, 1984, ch. 4, sect. 6, pp. 530-538.
- 19 Acetylferrocene, SDBS no. 7071; https://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology, accessed on September 24, 2018).
- 20 a) U. Salzner, J. Chem. Theory Comput., 2013, 9, 4064; b) D.
 R. Scott and R. S. Becker, J. Chem. Phys., 1961, 35, 516.
- 21 M. Zeller, M. W. Lufaso, L. Curtin and A. D. Hunter, Private communication to CSD (refcode: BIWKEX11).
- 22 J. A. Adeleke and L.-K. Liu, Acta Crystallogr., Sect. C: Crystal Struct. Commun., 1993, 49, 680.
- 23 P. Štěpnička, I. Císařová and R. Gyepes, *Eur. J. Inorg. Chem.,* 2006, 926.
- 24 W. H. Hersh, J. Chem. Educ., 1997, 74, 1485.
- 25 M. Zábranský, I. Císařová and P. Štěpnička, *Organometallics*, 2018, **37**, 1615.
- 26 A search in the Cambridge Structural Database, version 5.39 of November 2017 with updates from November 2017 and from February, May and August 2018 resulted in 58 structures (59 fragments) of this type of which 44 showed tilting by less than 2°.
- 27 Replacement of 4-tolyl substituents (R) in $[Pd(\mu-Cl)Cl(PR_3-\kappa P)]_2$ with 2-tolyl substituents induces bending of the planar structure by ca. 33°: a) S. Pratihar, J. Marek and S. Roy, *Inorg. Chim. Acta*, 2011, **372**, 362; b) S. Vuoti, J. Autio, M. Laitila, M. Haukka and J. Pursiainen, *Eur. J. Inorg. Chem.*, 2008, 397.
- 28 J. N. Smith, J. M. Hook and N. T. Lucas, J. Am. Chem. Soc., 2018, 140, 1131.
- 29 a) T. G. Appleton, H. C. Clark and L. E. Manzer, *Coord. Chem. Rev.*, 1973, **10**, 335; b) F. R. Hartley, *Chem. Soc. Rev.*, 1973, **2**, 163.
- 30 DFT studies on ferrocene amides have shown that rotation of the C=O bond from the cyclopentadienyl plane by 20° results in only a minor energy increase and minimally reduces orbital interaction of the conjugated moieties: a) L. Lin, A. Berces and H.-B. Kraatz, J. Organomet. Chem., 1998, 556, 11;

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C25

View Article Online

b) T. A. Fernandes, H. Solařová, I. Císařová, F. Uhlík, M. Štícha and P. Štěpnička, *Dalton Trans.*, 2015, **44**, 3092.

- 31 J. Vicente, A. Arcas, D. Bautista and P. G. Jones, *Organometallics*, 1997, **16**, 2127.
- 32 Selected examples: a) J.-F. Ma and Y. Yamamoto, Inorg. Chim. Acta, 2000, 299, 164; b) J. Tauchman, I. Císařová and P. Štěpnička, Organometallics, 2009, 28, 3288; c) P. Štěpnička, J. Schulz, T. Klemann, U. Siemeling and I. Císařová, Organometallics, 2010, 29, 3187; d) J. Schulz, I. Císařová and P. Štěpnička, Organometallics, 2012, 31, 729; e) H. Charvátová, I. Císařová and P. Štěpnička, Eur. J. Inorg. Chem., 2017, 288; f) M. Zábranský, A. Machara, I. Císařová and P. Štěpnička, Eur. J. Inorg. Chem., 2017, 4850 and refs. 11f, 12.
- 33 Ethyl acetate, SDBS no. 889; https://stbbs/db/aistogの沪 (National Institute of Advanced Industrial Science and Technology, accessed on November 20, 2018).
- 34 C. Mattheis and P. Braunstein, J. Organomet. Chem., 2001, 621, 218.
- 35 a) P. Štěpnička, H. Solařová, M. Lamač and I. Císařová, J. Organomet. Chem., 2010, 695, 2423; b) P. Štěpnička, H. Solařová and I. Císařová, J. Organomet. Chem., 2011, 696, 3727; c) M. Zábranský, I. Císařová and P. Štěpnička, Eur. J. Inorg. Chem., 2017, 2557; d) H. Charvátová, T. Vašíček, I. Císařová and P. Štěpnička, 307; M. Zábranský, I. Císařová and P. Štěpnička, Organometallics, 2018, 37, 1615 and refs. 11g, 32b, 32d.
- 36 P. Štěpnička, M. Lamač and I. Císařová, Polyhedron, 2004, 23, 921.



Figure 4. Views of the complex molecules in the structures of 6a·2CHCl₃,6b·CHCl₃ and 6d.



Figure 5. View of the complex cations in the structures of 8a, $8b \cdot 1/4$ CHCl₃ and 9.

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Graphical abstract entry

Coordination of phosphinoferrocene ligands with O-donor substituents to Pd(II) is affected by the nature of the oxygen functions and may results in hemilabile species.



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