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Palladium (II) complexes with mono-oxide 1,1′-bis(diphenylphosphino)metallocene ligands [Fe(η^5-$C_5Me_4PPh_2$)-(η^5-$C_5Me_4P\{O\}Ph_2$)] and [Os(η^5-$C_5H_4PPh_2$)(η^5-$C_5H_4P\{O\}Ph_2$)]

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Abstract

The monoxides [Fe(η^5-$C_5Me_4PPh_2$)(η^5-$C_5Me_4P\{O\}Ph_2$)] (**1**) and [Os(η^5-$C_5H_4PPh_2$)(η^5-$C_5H_4P\{O\}Ph_2$)] (**2**) have been prepared by treatment of the corresponding diphosphines with CCl_4 and methanol.These ligands react with [$Pd(PhCN)_2Cl_2$] to give dichloride complexes of different structure.The dimeric complex [{Os(η^5-$C_5H_4PPh_2$)(η^5-$C_5H_4P\{O\}Ph_2$)}$PdCl(\mu\text{-}Cl)]_2$ (**4**) contains the monodentate *P*-coordinated osmocene ligand with the free $P\{O\}Ph_2$ group, while the octamethylferrocene ligand gives the chelate k^2-P,O complex [{Fe(η^5-$C_5Me_4PPh_2$)(η^5-$C_5Me_4P\{O\}Ph_2$)}$PdCl_2$] (**3**).The structures of **3** and **4** have been determined crystallographically.Treatment of **3** and **4** with silver salts in CH_2Cl_2 or acetonitrile leads to the corresponding dicationic complexes [{M(η^5-$C_5R_4PPh_2$)(η^5-$C_5R_4P\{O\}Ph_2$)}$Pd(MeCN)_x]^{2+}$ (**5**, M = Fe, R = Me; **6**, M = Os, R = H). Complex **5** decomposes upon isolation, in contrast **6** is rather stable, probably due to Os–Pd bonding. The dichlorides **3** and **4** catalyze catalytic amination of *p*-bromotoluene with *N*-(4-tolyl)morpholine with lower activity than (dppf)$PdCl_2$, however they perform comparable to (dppf)$PdCl_2$ activity in coupling of *p*-bromotoluene with *p*-methoxyphenyl boronic acid.

Keywords: Palladium; 1,1′-Bis(diphenylphosphino)metallocene monoxides; Amination; Cross-coupling

1. Introduction

In recent years a strong attention to the transition metal complexes with chelating diphosphine monoxide ligands has been attracted due to their possibility to be applied as catalysts for various processes [1]. Complexation of diphosphine monoxides to palladium has been recently investigated [2a,2b]. In particular, the reaction of sodium tetrachloropalladate with two equivalents of diphosphine monoxide gave the complexes [($Ph_2PXP\{O\}Ph_2)_2PdCl_2$] (X = CH_2, $(CH_2)_2$, $(CH_2)_3$, $(CH_2)_4$, [Fe(η^5-$C_5H_4)_2$]) with two ligands coordinated by phosphino group merely [2a]. However the equimolar interaction of [Fe(η^5-$C_5H_4PPh_2$)(η^5-$C_5H_4P\{O\}Ph_2$)]-(dppfO) with palladium salts to form the P,O-chelated palladium complex has not been reported yet. Though the chelate palladium complex can be obtained from the corresponding dioxide [Fe(η^5-$C_5H_4P\{O\}Ph_2)_2$] [3]. Attempts to synthesize the dicationic palladium complex by treating [$(dppfO)_2PdCl_2$] with silver salts resulted in the mixture of unidentified products [2a]. It has to be noted that the P,O-bidentate coordination favored over the P-monodentate mode only in the case of the BINAP

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monoxide [2b] to give the chelated palladium complex. The steric hindrance of the BINAP monoxide backbone arisen from its rigidity has been assumed to be responsible for the equilibrium observed.

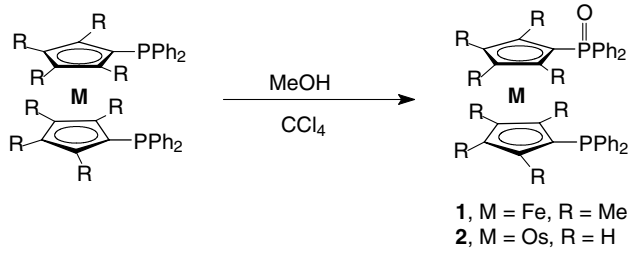
Here, we report about the synthesis of palladium complexes with [Fe(η^5-$C_5Me_4PPh_2$)(η^5-$C_5Me_4P\{O\}Ph_2$)] (**1**) and [Os(η^5-$C_5H_4PPh_2$)(η^5-$C_5H_4P\{O\}Ph_2$)] (**2**).

2. Results and discussion

The monoxide of 1,1′-bis(diphenylphosphino)ferrocene has been earlier prepared either by catalytic oxidation [1,4] or by oxidation with the mixture of CCl_4 and benzophenone [5]. The latter method has been previously utilized for synthesis of [Fe(η^5-$C_5Me_4PPh_2$)(η^5-$C_5Me_4P\{O\}Ph_2$)] (**1**) [5], though the low yields of less than 30% and necessity to purify **1** from the side organic products were disadvantages of this method. It has been found that methanol being used instead of benzophenone results in higher yields of **1**, up to 55%, and allows us easy work up of the reaction mixture (Scheme 1).

The 1,1′-bis(diphenylphosphino)osmocene gave in this reaction unknown earlier monoxide [Os(η^5-$C_5H_4PPh_2$)(η^5-$C_5H_4P\{O\}Ph_2$)] (**2**).

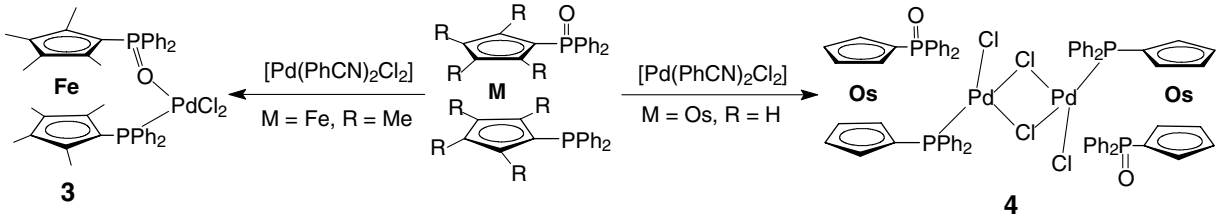
The new monoxide **2** has been characterized spectroscopically and by elemental analysis. In the $^{31}P\{^1H\}$ NMR spectrum of **2** two signals at δ −13.80, 28.95 arose from phosphine PPh_2 and phosphinoxide $P\{O\}Ph_2$ groups, correspondingly. In the ^1H NMR spectrum of **2** the Cp protons were observed as four singlets at δ 4.56, 4.69, 4.76 and 4.92, and the phenyl protons – as multiplets at δ 7.1–7.7. In its $^{13}C\{^1H\}$ NMR spectrum, six signals of the Cp carbons were in the region δ 67–76 and eight signals from two types of the phenyl rings were at δ 127–139.



Scheme 1.

Interaction of the monoxides **1** and **2** with [$Pd(PhCN)_2Cl_2$] were supposed to give κ^2-P,O chelated dichloride complexes [{M(η^5-$C_5R_4PPh_2$)(η^5-$C_5R_4P\{O\}Ph_2$)}$PdCl_2$] (**3**, M = Fe, R = Me; **4**, M = Os, R = H) while unexpectedly proceeded in diverse ways. In both reactions, **1** and **2** led to complexes which elemental analyses were consistent with the proposed dichlorides **3** and **4**. The ^1H and $^{13}C\{^1H\}$ NMR spectra showed two different types of Cp and Ph rings for both complexes **3** and **4**. Although in the $^{31}P\{^1H\}$ NMR spectra **3** and **4** differed significantly. Thus, in $^{31}P\{^1H\}$ NMR complex **4** showed signals at δ 28.27, 30.25, while complex **3** – at δ 17.75, 44.94. The upfield shifted signals corresponding to free ligands **1**, **2** dissapeared and instead new signals at δ 17.75 and δ 30.25 arose due to coordination of the PPh_2 group in complexes **3** and **4**. The downfield shift of the $P\{O\}Ph_2$ group from δ 30.65 in **1** to δ 44.94 in **3** may imply its coordination to palladium to form the chelated κ^2-P,O complex. On the other hand the chemical shifts of the $P\{O\}Ph_2$ group in **2** and **4** differ insignificantly, and the phosphinoxide group in **4** appeared to not coordinate to palladium to give the dimeric complex with bridging chlorides and monodentate κ^1-P bonded diphosphine oxides [{Os(η^5-$C_5H_4PPh_2$)(η^5-$C_5H_4P\{O\}Ph_2$)}$PdCl(\mu\text{-}Cl)]_2$ (Scheme 2).

The structures of **3** (Fig. 1) and **4** (Fig. 2) were determined by means of X-ray diffraction investigation (Table 1). Each of the palladium atoms in the dimeric complex **4** has slightly distorted square-planar configuration and coordinated to three chlorines and one phosphorus. The angle Cl(2)–Pd(1)–Cl(2A) is 83.23(9)° and similar to analogous complexes with other phosphines bearing two phenyl substituents [6a,6b]. The phosphine ligands are *trans* to each other with the bond lengths Pd(1)–P(2) of 2.229(2) Å. The dihedral angle between the plane Pd(1)Cl(2)Pd(1A)Cl(2A) and the Cp plane C(1)C(2)C(3)C(4)C(5) is 58°, and the osmocene moieties are situated up and under the plane Pd(1)Cl(2)Pd(1A)-Cl(2A). The bond length P═O is 1.495(7) Å and typical for the uncoordinated P═O bond. The P═O group is nearly in the plane of the Cp ring with the torsion angle O(1)P(1)C(1)C(5) of 18.3°. The analysis of crystal packing revealed that the P═O group participate in the C–H···O contacts (the distance H···O is 1.98–2.09 Å, the angle C–H···O is 154–164°) with solvate $CHCl_3$ molecules.



Scheme 2.

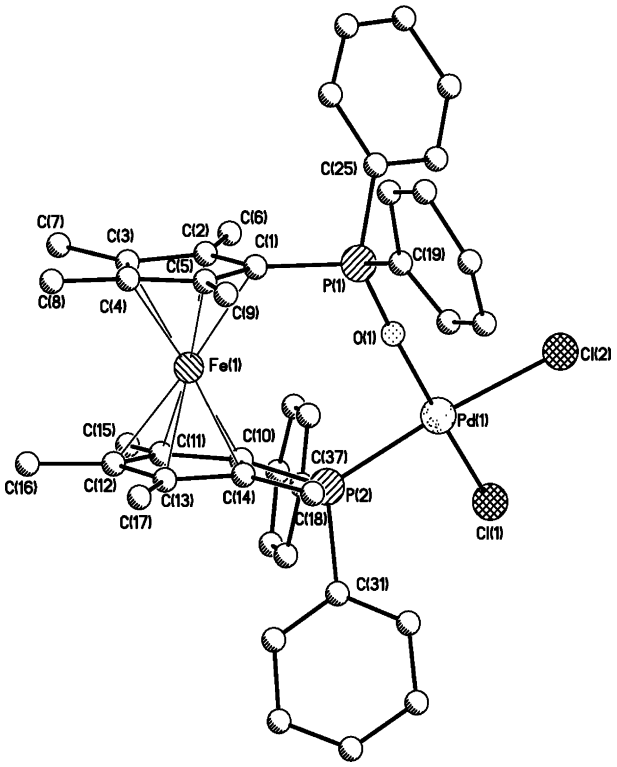


Fig. 1. The general view of **3**.

The palladium atom in **3** is coordinated with two terminal chlorides, phosphorus and oxygen (the Pd–O length is 1.998(9) Å) to give slightly distorted square-planar configuration. The P═O bond (1.479(9) Å) is slightly smaller than that for the coordinated (the length of the P═O bond in $[\{Fe(\eta^5\text{-}C_5H_4P\{O\}Ph_2)_2\}PdCl_2]$ is 1.495 Å [3]) and even the uncoordinated phosphinoxide group (the P═O length in **4** is 1.495(7) Å). The angle P(1)–O(1)–Pd(1) is 171° and significantly larger than the analogous angle for $[\{Fe(\eta^5\text{-}C_5H_4P\{O\}Ph_2)_2\}PdCl_2]$ (158.3°) [3] and $[\{Fe(\eta^5\text{-}C_5H_4PPh_2)(\eta^5\text{-}C_5H_4P\{O\}Ph_2)\}\text{-}W(CO)_3I]$ (160.2°) [7]. The coordination of the palladium to the oxygen of the phosphinoxide group occurred in expense of strong distortion of the ferrocene moiety. Thus, the phosphorus atom P(1) is inclined from the Cp plane outward the palladium on 0.0192 Å, while analogous value for the P(2) is much higher (0.5792 Å). Moreover the bond C(10)–P(2) is significantly bent out to the methyl C(18) with the angle C(10)–Cp_{center}(2)–P(2) of 11.0°, the analogous angle C(1)–Cp_{center}(1)–P(1) is only 2.0°. The distortions described result in the Cp rings to be fixed in unusual for the complexes with 1,1′-bis(diphenylphosphino)octamethylferrocene staggered conformation with the twisting angle C(1)–Cp_{center}(1)–Cp_{center}(2)–C(10) of 36.8°. The differences observed between the structures **3** and **4** are probably due to the presence of four α-methyls in the Cp rings in **3** that can hamper the dimerisation.

The reaction of the octamethylferrocene complex **3** with silver salts in the presence of water or acetonitrile led to partial oxidation of the ferrocene moiety resulting in mixture of unstable paramagnetic cationic complexes. The alternative approach that is the reaction of the free

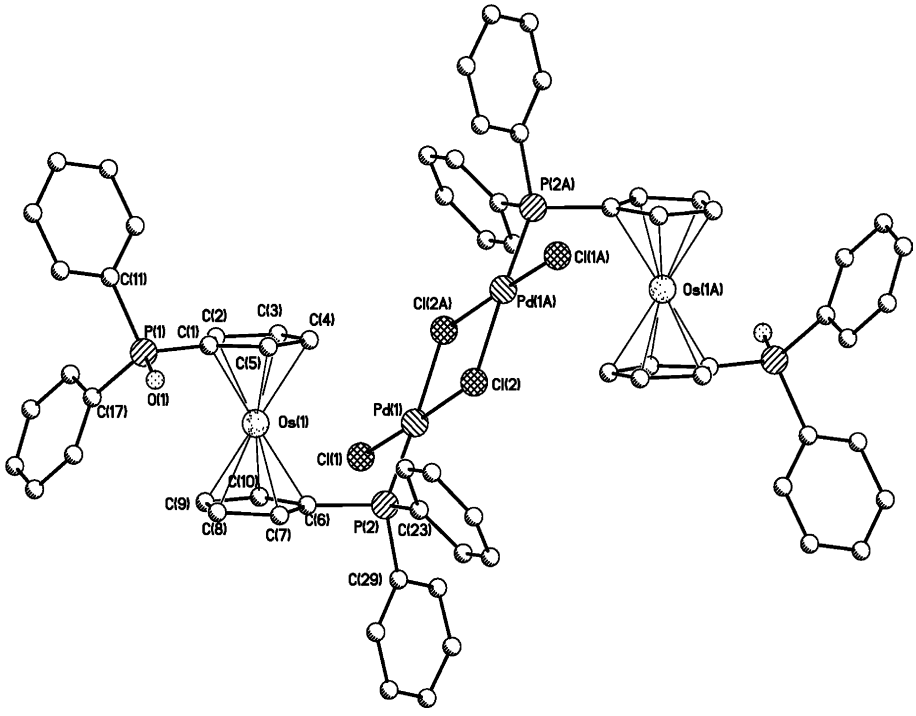


Fig. 2. The general view of **4**.

Table 1
Selected geometrical parameters for the complexes **3** and **4**

	3	**4**
	M = Fe	M = Os
M–C_{Cp} (Å)	2.03(1)–2.08(1)	2.16(1)–2.209(9)
M–X(1)[a] (Å)	1.669	1.811
M–X(2)[b] (Å)	1.656	1.822
Pd(1)–P(2) (Å)	2.264(3)	2.229(3)
Pd(1)–O(1) (Å)	1.998(9)	
Pd(1)–Cl(1) (Å)		
Pd(1)–Cl(1) (Å)	2.259(4)	2.283(2)
Pd(1)–Cl(2) (Å)	2.362(3)	2.326(2)
Pd(1)–Cl(2A) (Å)		2.428(2)
P(1)–O(1) (Å)	1.479(9)	1.495(7)
Pd(1)O(1)P(1) (°)	171.1(9)	
O(1)Pd(1)P(1) (°)	95.1(2)	
Cl(1)Pd(1)Cl(2) (°)	90.8(1)	
Cl(2)Pd(1)Cl(2A) (°)		83.23(9)
P(1)–C_{Cp} (Å)	1.78(1)	1.77(1)
P(2)–C_{Cp} (Å)	1.82(1)	1.794(9)
$\delta_{P(1)}$[c] (Å)	0.0192	0.0
$\delta_{P(2)}$[c] (Å)	0.570	−0.02
Cp/Cp[d] (°)	2.9	3.6
θ[e] (°)	36.8	15.8

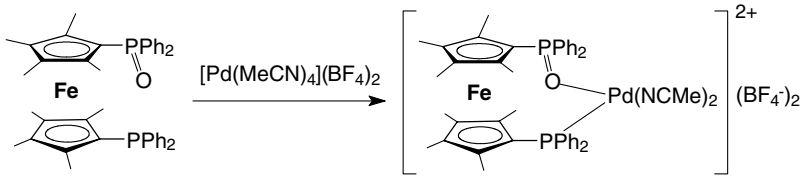
[a] Centroid of the C(1)–C(5) Cp ring.
[b] Centroid of the C(10)–C(15) Cp-ring in **3** and of C(6)–C(7) one in **4**.
[c] Deviation of the phosphorus atom from the Cp plane ring, a negative value meaning the P(1)/P(2) is closer to Os/Fe.
[d] The dihedral angle between the two Cp rings.
[e] The torsion angle $C_{Cp(1)}X(1)X(2)C_{Cp(2)}$, where X is the centroid of the corresponding Cp ring.

monoxide **1** with $[Pd(MeCN)_4](BF_4)_2$ allowed us to obtain the diamagnetic dication, which still underwent decomposition after removing the solvent in vacuum. The $^{31}P\{^1H\}$ NMR spectrum registered in 30 min. after addition of a solution $[Pd(MeCN)_4](BF_4)_2$ in CD_3CN to a solution of **1** in CD_2Cl_2 showed no signals of the starting material, instead new complex **5** having singlets at δ 32.70 and 53.77 formed. In the ^1H NMR spectrum of **5** methyls of the ferrocene moiety were presented by four singlets at δ 1.55, 1.76, 1.79 and 1.86, the signal corresponded to the coordinated acetonitrile arose at 2.00 and the multiplets at δ 7.3–7.8 were assigned to the phenyl protons. These spectral data allowed us to propose the chelated structure for $[\{Fe(\eta^5\text{-}C_5Me_4PPh_2)(\eta^5\text{-}C_5Me_4P\{O\}Ph_2)\}Pd(MeCN)_2]^{2+}(BF_4^-)_2$ (**5**), cf. Scheme 3.

The complex **5** is unstable without solvent. Evaporation of the reaction mixture following with dissolution of the residue in CD_3CN resulted in arising new signals in $^{31}P\{^1H\}$ NMR spectrum at δ 30.11, 34.35 50.12 and 51.50 of unidentified products together with the signals of **5**.

Treating the osmocene complex **4** with silver tosylate gave relatively stable dicationic aqua complex **6a**. Analogously, reaction of **4** with silver tetrafluoroborate in the presence of acetonitrile gave complex **6b** (Scheme 4).

Complexes **6a**,**b** were characterized by elemental analysis and spectroscopically. The $^{31}P\{^1H\}$ NMR spectra of **6a**,**b** are similar, and each consisted of two signals at δ 13.70, 48.98 (**6a**) and δ 16.59, 53.47 (**6b**) of the coordinated phosphinoxide and phosphino groups, correspondingly. In their ^1H NMR spectra the Cp protons are presented at δ 4.88, 5.79, 6.08, 6.88 (**6a**) and δ 5.16, 5.61, 5.79, 6.73 (**6b**). Such a large difference of chemical shifts in ^1H NMR of 1,1′-bis(phosphino)metallocene complexes between α- and β-Cp protons is indicative for the presence of M–Pd bonding [8]. Complex **6b** contains one molecule of acetonitrile according to integral intensity of the signal in ^1H NMR that confirms formation of the Os–Pd bond as well; otherwise it should contain two solvate ligands. Both the relatively large difference between the signals of α- and β-carbons of the



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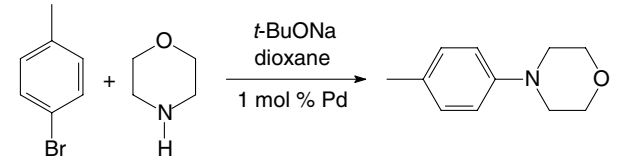
Scheme 3.

6a, L = H_2O, X = OTs
6b, L = MeCN, X = BF_4

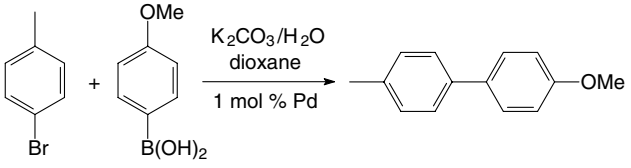
Scheme 4.

Cp rings (δ 74.49, 78.24, 78.34, 79.93 for **6a** and δ 74.94, 78.42, 78.94, 80.79 for **6b**) and significant upfield shift of the *ipso*-carbons of the Cp rings (δ 60.74 for **6a** and δ 59.80 for **6b**) in the $^{13}C\{^1H\}$ NMR spectrum can also be evident for the metal–metal bonding. The transformation of the bidentate osmocene ligand to the tridentate is probably responsible for the stabilization of the dicationic complexes **6a**,**b** in comparison to **5**.

The dichloride complexes **3** and **4** were tested in catalytic amination (Scheme 5) and Suzuki type reaction (Scheme 6) of *p*-bromotoluene. The amination of *p*-bromotoluene catalyzed by **3** and **4** gave lower yields comparing to 1,1′-bis(diphenylphosphino)ferrocene (Table 2). Though, the precursor **3** stabilized with octamethylferrocene ligand performed comparable activity to 1,1′-bis(diphenylphosphino)ferrocene in the reaction of *p*-bromotoluene with *p*-methoxyphenyl boronic acid to give 4-methoxy-4′-methylbiphenyl (Table 3), cf. Schemes 5 and 6.



Scheme 5.



Scheme 6.

Table 2
The catalytic amination of *p*-bromotoluene with *N*-(4-tolyl)-morpholine catalyzed by **3** and **4**

Run	Catalyst	Yield of *N*-(4-tolyl)-morpholine (%)
1	(dppf)$PdCl_2$	42
2	**3**	25
3	**4**	21

Conditions: 4-Bromotoluene (1 eq), morpholine (1.25 eq), *t*-BuONa (1.25 eq), catalyst (0.01 eq), dioxane (2.5 ml), T = 100 °C, t = 20 min.

Table 3
The catalytic reaction of *p*-bromotoluene with *p*-methoxyphenyl boronic acid catalyzed by **3** and **4**

Run	Catalyst	Yield of 4-methoxy-4′-methylbiphenyl (%)
1	(dppf)$PdCl_2$	60
2	**3**	71
3	**4**	38

Conditions: 4-Bromotoluene (1 eq), 4-methoxyphenylboronic acid (1.32 eq), K_2CO_3 (3 eq), catalyst (0.01 eq), dioxane (1.5 ml), water (0.5 ml), T = 100 °C, t = 10 min.

3. Experimental

3.1. General procedures

All experiments were performed under argon in solvents purified by standard methods. ^1H, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker AMX 400 and Varian VXR 400 spectrometers. Chemical shifts are reported in ppm (δ) with reference to TMS as an internal standard (^1H and $^{13}C\{^1H\}$ NMR spectra), and 85% H_3PO_4 for $^{31}P\{^1H\}$ NMR spectra as an external standards. Microanalyses were performed at the A.N. Nesmeyanov Institute of Organoelement Compounds. The following compounds were synthesized according to published procedures: $[Pd(PhCN)_2Cl_2]$ [9], $[Fe(\eta^5\text{-}C_5Me_4PPh_2)_2]$ [5], $[Os(\eta^5\text{-}C_5H_4PPh_2)_2]$ [8].

3.2. Synthesis of $[Fe(\eta^5\text{-}C_5Me_4PPh_2)(\eta^5\text{-}C_5Me_4P\{O\}Ph_2)]$ (**1**)

To a solution of $[Fe(\eta^5\text{-}C_5Me_4PPh_2)_2]$ (1.00 g, 1.5 mmol) in benzene (50 mL) methanol (0.5 mL) and CCl_4 (7 mL) were added. The mixture was heated at 50 °C for 1.5 h. The solution was then cooled to room temperature and passed through a bed of silica (5 cm). The unreacted diphosphine $[Fe(\eta^5\text{-}C_5Me_4PPh_2)_2]$ (0.28 g) was eluted first with benzene, then the monoxide **1** was eluted with the mixture Et_2O/benzene (2:1). Yield of **1**: 0.54 g (53%). Anal. Calcd. for $C_{42}H_{44}FeOP_2$: C, 73.90; H, 6.50. Found: C, 73.91; H, 6.61%. ^1H NMR ($CDCl_3$): δ 1.38 (s, 3H, C_5Me_4); 1.39 (s, 3H, C_5Me_4); 1.84 (s, 3H, C_5Me_4); 1.97 (s, 3H, C_5Me_4); 7.1–7.4 (m, 16H, Ph); 7.52 (dd, 4H, *o*-H(Ph), $^3J_{HH}$ = 7.3, $^3J_{HP}$ = 11.6 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −21.59 (s, PPh_2); 30.65 (s, $P\{O\}Ph_2$).

3.3. Synthesis of $[Os(\eta^5\text{-}C_5H_4PPh_2)(\eta^5\text{-}C_5H_4P\{O\}Ph_2)]$ (**2**)

To a solution of $[Os(\eta^5\text{-}C_5H_4PPh_2)_2]$ (0.78 g, 1.13 mmol) in benzene (50 mL) methanol (0.3 mL) and CCl_4 (5 mL) were added. The mixture was heated at 40 °C for 40 min. The solution was cooled to room temperature and then passed through a bed of silica (5 cm). The unreacted $[Os(\eta^5\text{-}C_5H_4PPh_2)_2]$ (0.47 g) was eluted with benzene, the monoxide **2** – with the mixture acetone/CH_2Cl_2 (1:1). Yield of **2**: 0.26 g (33%). Anal. Calcd. for $C_{34}H_{28}OOsP_2$: C, 57.94; H, 4.00. Found: C, 58.15; H, 4.31%. ^1H NMR ($CDCl_3$): δ 4.56 (s, 2H, C_5H_4); 4.69 (s, 2H, C_5H_4); 4.76 (s, 2H, C_5H_4); 4.92 (s, 2H, C_5H_4); 7.26 (m, 10H, Ph); 7.40 (m, 4H, Ph); 7.48 (t, 2H, *p*-H(Ph), $^3J_{HH}$ = 7.6 Hz); 7.61 (dd, 4H, *o*-H(Ph), $^3J_{HH}$ = 7.2, $^3J_{HP}$ = 12.2 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 67.49 (d, α-C(C_5H_4); $^2J_{CP}$ = 12.6 Hz); 68.85 (d, β-C(C_5H_4); $^3J_{CP}$ = 9.6 Hz); 69.82 (d, β-C(C_5H_4);

$^3J_{CP}$ = 3.3 Hz); 70.74 (d, *ipso*-C(C_5H_4); $^1J_{CP}$ = 114.5 Hz); 70.98 (d, α-C(C_5H_4); $^2J_{CP}$ = 15.6 Hz); 75.37 (d, *ipso*-C(C_5H_4); $^1J_{CP}$ = 9.9 Hz); 127.85 (d, *o*-C(Ph), $^2J_{CP}$ = 7.0 Hz); 127.88 (s, *p*-C(Ph)); 128.22 (d, *m*-C(Ph), $^3J_{CP}$ = 18.1 Hz); 131.32 (d, *m*-C(Ph), $^3J_{CP}$ = 9.9 Hz); 131.38 (s, *p*-C(Ph)); 133.45 (d, *o*-C(Ph), $^2J_{CP}$ = 19.0 Hz); 134.43 (d, *ipso*-C(Ph), $^1J_{CP}$ = 106.5 Hz); 138.75 (d, *ipso*-C(Ph), $^1J_{CP}$ = 9.2 Hz); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −13.80 (s, PPh_2); 28.63 (s, P{O}Ph_2).

3.4. Synthesis of [{Fe(η⁵-$C_5Me_4PPh_2$)(η⁵-C_5Me_4P{O}-Ph_2}$PdCl_2$)] (3)

To a solution of [Pd(PhCN)$_2$Cl$_2$] (0.69 g, 1.80 mmol) in benzene (100 mL) a solution of **1** (1.23 g, 1.80 mmol) in benzene (250 mL) was added dropwise at room temperature. The reaction mixture was stirred for 18 h. The precipitate was filtered off, washed with benzene and recrystallized from hexane–CH_2Cl_2. Yield of **3**: 1.51 g (97%). Anal. Calcd. for $C_{42}H_{44}Cl_2FeOP_2Pd$-CH_2Cl_2: C, 51.32; H, 4.70. Found: C, 51.74; H, 4.52%. ^1H NMR ($CDCl_3$): δ 1.46 (s, 3H, C_5Me_4); 1.50 (s, 3H, C_5Me_4); 1.64 (s, 3H, C_5Me_4); 7.28 (m, 4H, Ph); 7.44 (m, 8H, Ph); 7.84 (dd, 4H, *o*-H(Ph), $^3J_{HH}$ = 7.8, $^3J_{HP}$ = 11.3 Hz); 8.06 (m, 4H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 8.78 (s, C_5Me_4); 8.92 (s, C_5Me_4); 12.39 (s, C_5Me_4); 12.97 (s, C_5Me_4); 68.17 (d, *ipso*-C(C_5Me_4), $^1J_{CP}$ = 23.5 Hz); 68.97 (d, *ipso*-C(C_5Me_4), $^1J_{CP}$ = 37.9 Hz); 85.14 (d, β-C(C_5Me_4), $^3J_{CP}$ = 8.0 Hz); 85.34 (d, α-C(C_5Me_4), $^2J_{CP}$ = 13.2 Hz); 86.53 (d, β-C(C_5Me_4), $^3J_{CP}$ = 6.0 Hz); 87.05 (d, α-C(C_5Me_4), $^2J_{CP}$ = 11.2 Hz); 127.68 (d, *m*-C(Ph), $^3J_{CP}$ = 7.0 Hz); 128.48 (d, *m*-C(Ph), $^3J_{CP}$ = 12.8 Hz); 129.85 (d, *ipso*-C(Ph), $^1J_{CP}$ = 56.7 Hz); 130.80 (d, *p*-C(Ph), $^4J_{CP}$ = 2.0 Hz); 130.91 (d, *ipso*-C(Ph), $^1J_{CP}$ = 7.0 Hz); 132.11 (d, *p*-C(Ph), $^4J_{CP}$ = 2.8 Hz); 132.54 (d, *o*-C(Ph), $^2J_{CP}$ = 10.8 Hz); 135.71 (d, *o*-C(Ph), $^2J_{CP}$ = 10.4 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 17.75 (s, PPh_2); 44.94 (s, P{O}Ph_2).

3.5. Synthesis of [{Os(η⁵-$C_5H_4PPh_2$)(η⁵-C_5H_4P{O}-Ph_2)}$PdCl(\mu$-$Cl)]_2$ (4)

A solution of **2** (0.72 g, 1.02 mmol) in benzene (150 mL) was added dropwise to a solution of [Pd(PhCN)$_2$Cl$_2$] (0.39 g, 1.02 mmol) in benzene (50 mL) at room temperature. The solution was stirred for 18 h. The benzene solution was concentrated to 10 mL and then treated with hexane (50 mL). The precipitate was filtered off, washed with hexane and dried in vacuum. Yield of **4**: 0.88 g (98%). Anal. Calcd. for $C_{68}H_{56}Cl_4O_2Os_2P_4Pd_2 \cdot C_6H_6$: C, 48.24; H, 3.39; Os, 20.65. Found: C, 47.94; H, 3.69; Os, 20.34%. ^1H NMR ($CDCl_3$): δ 4.94 (s, 2H, C_5H_4); 4.99 (s, 2H, C_5H_4); 5.16 (s, 2H, C_5H_4); 5.66 (s, 2H, C_5H_4); 7.30 (m, 4H, Ph); 7.37–7.60 (m, 12H, Ph); 7.66 (dd, 4H, *o*-H(Ph), $^3J_{HH}$ = 7.5, $^3J_{HP}$ = 11.8 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 66.10 (d, *ipso*-C(C_5H_4); $^1J_{CP}$ = 67.5 Hz); 69.76 (d, α-C(C_5H_4); $^2J_{CP}$ = 12.2 Hz); 71.13 (d, β-C(C_5H_4); $^3J_{CP}$ = 5.5 Hz); 71.76 (d, α-C(C_5H_4); $^2J_{CP}$ = 11.0 Hz); 72.98 (d, *ipso*-C(C_5H_4); $^1J_{CP}$ = 117.6 Hz); 73.04 (d, β-C(C_5H_4); $^3J_{CP}$ = 9.9 Hz); ∼127.9 (d, overlapped, *ipso*-C(Ph), $^1J_{CP}$ ∼ 60 Hz); 128.02 (d, *m*-C(Ph), $^3J_{CP}$ = 12.1 Hz); 128.22 (d, *m*-C(Ph), $^3J_{CP}$ = 11.9 Hz); 131.35 (d, *o*-C(Ph), $^2J_{CP}$ = 9.8 Hz); 131.60 (s, *p*-C(Ph)); 131.76 (s, *p*-C(Ph)); 133.25 (d, *ipso*-C(Ph), $^1J_{CP}$ = 106.7 Hz); 133.58 (d, *o*-C(Ph), $^2J_{CP}$ = 10.8 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 28.27 (s, P{O}Ph_2); 30.25 (s, PPh_2).

3.6. Interaction of [Fe(η⁵-$C_5Me_4PPh_2$)(η⁵-C_5Me_4P{O}-Ph_2)] with [Pd(MeCN)$_4$](BF_4)$_2$

A solution of **1** (14 mg, 0.02 mmol) in CD_2Cl_2 (1 mL) was added dropwise at 0 °C to a solution of [Pd(MeCN)$_4$](BF$_4$)$_2$ (9 mg, 0.02 mmol) in CD_3CN (0.3 mL) with stirring. The reaction mixture was allowed to warm to room temperature and stirred for 30 min. $^{31}P\{^1H\}$ NMR: δ 32.70 (s); 53.77 (s). ^1H NMR: δ 1.55 (s, 3H, C_5Me_4); 1.76 (s, 3H, C_5Me_4); 1.79 (s, 3H, C_5Me_4); 1.86 (s, 3H, C_5Me_4); 2.00 (s, 6H, 2CH_3CN); 7.41 (m, 8H, Ph); 7.55 (m, 8H, Ph); 7.72 (m, 4H, Ph).

3.7. Synthesis of [{Os(η⁵-$C_5H_4PPh_2$)(η⁵-C_5H_4P{O}-Ph_2)}$Pd(H_2O)](OTs)_2$ (6a)

To a solution of **4** (0.23 g, 0.13 mmol) in CH_2Cl_2 (30 mL) cooled to 0 °C silver tosylate (0.15 g, 0.52 mmol) was added with stirring. The mixture was allowed to warm to room temperature and stirred for 4 h. Precipitate of silver chloride was filtered off, the filtrate was concentrated to 3 mL and quenched with Et_2O (30 mL) to give yellow–brown precipitate, which was filtered off, washed with Et_2O and dried in vacuum. Yield of **6a**: 0.29 g (97%). Anal. Calcd. for $C_{48}H_{44}O_8Os$-P_2PdS_2: C, 49.21; H, 3.78; Os, 16.24. Found: C, 49.76; H, 3.99; Os, 16.17%. ^1H NMR ($CDCl_3$): δ 2.30 (s, 6H, *p*-$CH_3C_6H_4SO_3$); 4.88 (s, 2H, C_5H_4); 5.79 (s, 2H, C_5H_4); 6.08 (s, 2H, C_5H_4); 6.88 (s, 2H, C_5H_4); 7.06 (d, 4H, *p*-$CH_3C_6H_4SO_3$, $^3J_{HH}$ = 7.2 Hz); 7.49 (m, 8H, Ph); 7.61 (m, 4H, Ph); 7.76 (m, 8H, Ph); 7.91 (dd, 4H, *o*-H(Ph), $^3J_{HH}$ = 7.6, $^3J_{HP}$ = 13.4 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 21.14 (s, *p*-$CH_3C_6H_4SO_3$); 60.74 (d, *ipso*-C(C_5H_4); $^1J_{CP}$ = 56.3 Hz); 74.49 (d, α-C(C_5H_4); $^2J_{CP}$ = 10.8 Hz); 75.40 (d, *ipso*-C(C_5H_4); $^1J_{CP}$ = 107.4 Hz); 78.24 (d, β-C(C_5H_4); $^3J_{CP}$ = 8.8 Hz); 78.34 (d, α-C(C_5H_4); $^2J_{CP}$ = 11.1 Hz); 79.89 (d, β-C(C_5H_4); $^3J_{CP}$ = 8.4 Hz); 122.24 (d, *ipso*-C(Ph), $^1J_{CP}$ = 62.7 Hz); 126.25 (s, *o*-C or *m*-C, *p*-$CH_3C_6H_4SO_3$); 127.66 (d, *ipso*-C(Ph),

$^1J_{CP}$ = 111.4 Hz); 128.72 (s, *o*-C or *m*-C, *p*-$CH_3C_6H_4SO_3$); 129.36 (d, *m*-C(Ph), $^3J_{CP}$ = 13.1 Hz); 129.52 (d, *m*-C(Ph), $^3J_{CP}$ = 12.8 Hz); 131.61 (d, *o*-C(Ph), $^2J_{CP}$ = 11.2 Hz); 133.09 (d, *p*-C(Ph), $^4J_{CP}$ = 2.4 Hz); 133.65 (d, *p*-C(Ph), $^4J_{CP}$ = 2.8 Hz); 134.84 (d, *o*-C(Ph), $^2J_{CP}$ = 12.4 Hz); 140.32 (s, *ipso*-C, *p*-CH_3-$C_6H_4SO_3$); 142.41 (s, *ipso*-C, *p*-$CH_3C_6H_4SO_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 13.69 (s, PPh_2); 48.98 (s, $P\{O\}Ph_2$).

3.8. Synthesis of [{Os(η^5-$C_5H_4PPh_2$)(η^5-$C_5H_4P\{O\}Ph_2$)}Pd(MeCN)](BF$_4$)$_2$ (**6b**)

To a solution of **4** (0.20 g, 0.11 mmol) in CH_2Cl_2 (30 mL) at 0 °C acetonitrile (0.1 mL) and silver tetrafluoroborate (0.09 g, 0.46 mmol) were added. The reaction mixture was allowed to warm to room temperature and stirred for 4 h. Silver chloride was filtered off, the filtrate was concentrated to 3 mL and then quenched with Et_2O (30 mL). The precipitate was filtered off, washed with Et_2O and dried. Yield of **6b**: 0.23 g (98%). Anal. Calcd. for $C_{36}H_{31}B_2F_8NOOsP_2Pd2\cdot CH_2Cl_2$: C, 38.17; H, 2.95. Found: C, 38.46; H, 2.86%. ^1H NMR (CD_2Cl_2): δ 2.23 (s, 3H, MeCN); 5.16 (s, 2H, C_5H_4); 5.61 (s, 2H, C_5H_4); 5.79 (s, 2H, C_5H_4); 6.73 (s, 2H, C_5H_4); 7.5–7.9 (m, 20H, Ph). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 2.98 (s, CH_3CN); 59.80 (d, *ipso*-C(C_5H_4); $^1J_{CP}$ = 56.7 Hz); 74.94 (d, α-C(C_5H_4); $^2J_{CP}$ = 11.2 Hz); 75.83 (d, *ipso*-C(C_5H_4); $^1J_{CP}$ = 56.7 Hz); 78.42 (d, α-C(C_5H_4); $^2J_{CP}$ = 10.8 Hz); 78.94 (d, β-C(C_5H_4); $^3J_{CP}$ = 8.8 Hz); 80.76 (d, β-C(C_5H_4); $^3J_{CP}$ = 8.8 Hz); 120.77 (s, CH_3C N); 122.35 (d, *ipso*-C(Ph); $^1J_{CP}$ = 65.4 Hz); 126.91 (d, *ipso*-C(Ph); $^1J_{CP}$ = 111.0 Hz); 129.74 (d, *m*-C(Ph), $^3J_{CP}$ = 13.2 Hz); 130.30 (d, *m*-C(Ph), $^3J_{CP}$ = 12.8 Hz); 131.71 (d, *o*-C(Ph), $^2J_{CP}$ = 11.2 Hz); 134.26 (d, *o*-C(Ph), $^2J_{CP}$ = 12.8 Hz); 134.59 (d, *p*-C(Ph), $^4J_{CP}$ = 3.2 Hz); 137.72 (d, *p*-C(Ph), $^4J_{CP}$ = 2.4 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 16.59 (s, PPh_2); 53.48 (s, $P\{O\}Ph_2$).

3.9. Catalytic amination of 4-bromotoluene with morpholine

4-Bromotoluene (117 mg 0.684 mmol), morpholine (75 mg, 0.850 mmol), sodium *tert*-butoxide (81 mg, 0.850 mmol) and 1 mol% palladium catalyst were stirred in dioxane (2.5 ml) under reflux during appropriate time. The reaction mixture was quenched with water and twice extracted with CH_2Cl_2. The organic layer was then dried over Na_2SO_4 and concentrated in vacuo. The yield of *N*-(4-tolyl)-morpholine was determined by NMR, using acetylferrocene as a standard. ^1H NMR ($CDCl_3$): δ 2.26 (s, 3H, CH_3); 3.08 (m, 4H, CH_2); 3.84 (m, 4H, CH_2); 6.81 (m, 2H, C_6H_4); 7.07 (m, 2H, C_6H_4).

3.10. Cross-coupling of 4-bromotolune with 4-methoxyphenylboronic acid

4-Bromotoluene (50 mg 0.292 mmol), 4-methoxyphenylboronic acid (59 mg, 0.385 mmol), potassium carbonate (121 mg, 0.877 mmol) and 1 mol% palladium catalyst in the mixture of dioxane (1.5 ml) and water (0.5 ml) were stirred under reflux during 10 min. The reaction mixture was quenched with water and twice extracted with CH_2Cl_2. The organic layer was then dried over Na_2SO_4 and concentrated in vacuo. The yield of 4-methoxy-4′-methylbiphenyl was determined by NMR, using acetylferrocene as a standard. ^1H NMR ($CDCl_3$): δ 2.36 (s, 3H, CH_3); 3.81 (s, 3H, OCH_3); 6.94 (m, 2H, C_6H_4); 7.20 (m, 2H, C_6H_4); 7.42 (m, 2H, C_6H_4); 7.48 (m, 2H, C_6H_4).

3.11. X-ray structure determination

Crystals of **3** suitable for X-ray analysis were obtained by slow diffusion of hexane into a solution of the complex in dichloromethane. Crystals of **4** were obtained by slow evaporation of a solution of the complex in chloroform. X-ray diffraction experiments for **3** and **4** were carried out with a Bruker SMART 1000 CCD area detector, using graphite monochromated Mo Kα radiation (λ = 0.71073 Å, ω-scans with a 0.3° step in and 10 s per frame exposure) at 110 K. Reflection intensities were integrated using SAINT software [10] and semi-empirical method SADABS [11]. The structures were solved by direct method and refined by the full-matrix least-squares against F^2 in anisotropic approximation for no-hydrogen atoms. The analysis of systematic absences as well as the R_{int} value have revealed that despite β is close to 90° the crystal of **3** is monoclinic. The inclusion of twining law (TWIN 0 1 0 1 0 0 0 0 −1) lead to significant decrease of the *R*-factor (BASF parameter was equal to 0.407), thus we can conclude that **3** is a twin. All hydrogen atoms were placed in geometrically calculated positions and included in final the refinement using the ''riding'' model with the U_{iso}(H) parameters equal to 1.2 $U_{eq}(C_i)$ or 1.5 $U_{eq}(C_{ii})$, where $U(C_i)$ and $U(C_{ii})$ are respectively the equivalent thermal parameters of the methyne and methylene carbon atoms to which corresponding H atoms are bonded. Crystal data and structure refinement parameters for **3** and **4** are given in Table 4. All calculations were performed on an IBM PC/AT using the SHELXTL software [12].

4. Supplementary material

The crystallographic data have been deposited with the Cambridge Crystallographic Data Center, CCDC 258452 for **3** and CCDC 258452 for **4**. Copies of this

Table 4
Crystallographic data for complexes **3** and **4**

	3	**4**
Formula	$C_{42}H_{44}C_{12}FeOP_2Pd \cdot 2CH_2Cl_2$	$C_{68}H_{56}Cl_4O_2Os_2P_4Pd_2 \cdot 8CHCl_3$
T (K)	120	120
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$
a (Å)	11.036(4)	18.040(4)
b (Å)	20.389(5)	10.417(3)
c (Å)	20.005(5)	26.220(5)
β (°)	90.485(5)	104.955(4)
V (Å)^3, Z	4501(2), 4	4760.2(19), 2
M	1029.71	2718.95
μ (cm^{-1})	11.82	39.29
$F(000)$	2008	2632
d_{calc} (g cm^{-3})	1.520	1.897
$2\theta_{max}$ (°)	50	52
No. of reflections measured (R_{int})	25,297 (0.0761)	30,297 (0.0686)
No. of independent reflections	7850	9313
No. of reflections with $I > 2\sigma(I)$	3599	6051
No. of parameters	517	514
R_1	0.0834	0.0602
wR_2	0.1834	0.1645
GOF	1.017	0.981
Max./Min. peak (e Å^{-3})	1.27/−0.946	1.71/−1.71

information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

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