Synthesis and structures of 1,1′-bis(diphenylphosphino)metallocenyl complexes $M(\eta^5\text{-}C_5H_4PPh_2)_2Ru(H_2O)_2(OTs)_2$ (M = Fe, Ru, or Os)

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The reaction of equimolar amounts of $M(\eta^5\text{-}C_5H_4PPh_2)_2$ (M = Fe, Ru, or Os) and $[Ru(H_2O)_6](OTs)_2$ afforded the $M(\eta^5\text{-}C_5H_4PPh_2)_2Ru(H_2O)_2(OTs)_2$ complexes, which were characterized by elemental analysis and ^1H, ^{13}C, and ^{31}P NMR spectroscopy. The structure of the osmocene complex was established by X-ray diffraction.

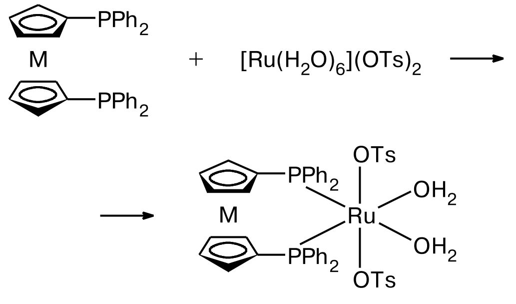
Key words: 1,1′-bis(diphenylphosphino)metallocene, complexes, ruthenium, iron, osmium.

Chelate di- and triphosphine ruthenium complexes belong to an important class of coordination compounds. Earlier,[1] we have demonstrated that the *cis*-$[Ru(Ph_2P\{CH_2\}_2PPh_2)_2(OTs)]OTs$ and $RuPhP(CH_2CH_2CH_2PPh_2)_2(OTs)_2$ complexes catalyze alternating copolymerization of ethylene with carbon monoxide.

In the present study, we synthesized ruthenium complexes with the 1,1′-bis(diphenylphosphino)metallocenyl ligands. We used 1,1′-bis(diphenylphosphino)metallocenyl complexes as ligands taking into account the following fact. Earlier, it has been demonstrated that palladium complexes with these ligands exhibit high chemoselectivity due to their ability to form the M—Pd bond[2—5] and, in some cases, these complexes are superior to complexes with organic diphosphines in activity.[6]

The reaction of equimolar amounts of 1,1′-bis(diphenylphosphino)metallocene and $[Ru(H_2O)_6](OTs)_2$ (Scheme 1) afforded the $M(\eta^5\text{-}C_5H_4PPh_2)_2Ru(H_2O)_2(OTs)_2$ complexes (M = Fe (**1**), Ru (**2**), or Os (**3**)), which were characterized by elemental analysis and ^1H, ^{13}C, and ^{31}P NMR spectroscopy.

Scheme 1



1—3

M = Fe (**1**), Ru (**2**), Os (**3**)

The ^{31}P NMR spectra of compounds **1—3** show singlets at δ 58.1 (**1**), 54.7 (**2**), and 58.1 (**3**), which is indicative of the presence of the symmetry plane in these molecules. The cyclopentadienyl ligands are characterized by pairs of broadened singlets at δ 4.18 and 4.26 (**1**), 4.61 and 4.65 (**2**), and 4.81 and 4.87 (**3**) in the ^1H NMR spectra and pairs of singlets and triplets for the quaternary carbon atoms at δ 70—80 in the ^{13}C NMR spectra. The ^1H and ^{13}C NMR spectra provide evidence for the presence of two tosylate residues in each molecule, as follows from the presence of pairs of doublets at δ 7.08 and 7.29 (**1**), 7.08 and 7.29 (**2**), and 7.08 and 7.28 (**3**) and four singlets at δ 125—141. The phenyl rings at the phosphorus atoms appear as three multiplets at δ 7.2—7.6 in the ^1H NMR spectra and four signals at δ 125—140 in the ^{13}C NMR spectra, the signals for the quaternary carbon atom and the signals for the C atoms in the *meta* and *ortho* positions being decoupled from the phosphorus atoms. The signals for the protons of water molecules are not observed in the ^1H NMR spectra due, apparently, to their rapid exchange.

The structure of complex **3** was studied by X-ray diffraction (Fig. 1, Table 1). The cyclopentadienyl groups in osmocene **3** adopt a staggered conformation with the P(1)—C(1)—C(6)—P(2) pseudotorsion angle of −37.4°. The Cp rings are inclined toward the ruthenium atom (dihedral angle is 6.0°). The phosphorus atoms deviate from the plane of the Cp groups toward the metal atom by 0.21 and 0.14 Å.

The ruthenium atom in molecule **3** has a distorted octahedral coordination (Fig. 2). The ruthenium and osmium atoms are at a nonbonded distance (4.330(1) Å).

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Table 1. Selected bond length (*d*) and bond angles (ω) in molecule **3**

Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å
Os(1)—C(1)	2.143(5)	Os(1)—C(3)	2.208(5)	S(1)—O(3)	1.436(4)
Os(1)—C(6)	2.148(4)	Os(1)—C(9)	2.217(5)	S(1)—O(2)	1.449(4)
Os(1)—C(5)	2.165(5)	Ru(1)—O(4)	2.114(3)	S(1)—O(1)	1.490(3)
Os(1)—C(2)	2.174(5)	Ru(1)—O(1)	2.145(3)	S(1)—C(35)	1.769(5)
Os(1)—C(10)	2.182(5)	Ru(1)—O(2W)	2.190(3)	S(2)—O(5)	1.443(5)
Os(1)—C(7)	2.184(5)	Ru(1)—O(1W)	2.222(3)	S(2)—O(6)	1.440(5)
Os(1)—C(8)	2.194(5)	Ru(1)—P(1)	2.2544(13)	S(2)—O(4)	1.464(4)
Os(1)—C(4)	2.201(5)	Ru(1)—P(2)	2.2926(13)	S(2)—C(42)	1.763(6)
Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
O(4)—Ru(1)—O(1)	171.30(12)	P(1)—Ru(1)—P(2)	97.84(5)	O(3)—S(1)—O(1)	111.8(2)
O(4)—Ru(1)—O(2W)	86.77(13)	C(1)—P(1)—C(17)	104.9(2)	O(2)—S(1)—O(1)	110.8(2)
O(1)—Ru(1)—O(2W)	85.17(13)	C(1)—P(1)—C(11)	102.1(2)	O(3)—S(1)—C(35)	107.0(2)
O(4)—Ru(1)—O(1W)	86.34(14)	C(17)—P(1)—C(11)	102.3(2)	O(2)—S(1)—C(35)	108.1(2)
O(1)—Ru(1)—O(1W)	88.92(13)	C(1)—P(1)—Ru(1)	118.02(16)	O(1)—S(1)—C(35)	104.2(2)
O(2W)—Ru(1)—O(1W)	79.10(13)	C(17)—P(1)—Ru(1)	118.93(17)	O(5)—S(2)—O(6)	115.8(4)
O(4)—Ru(1)—P(1)	94.83(10)	C(11)—P(1)—Ru(1)	108.17(15)	O(5)—S(2)—O(4)	109.5(3)
O(1)—Ru(1)—P(1)	89.04(9)	C(6)—P(2)—C(23)	98.8(2)	O(6)—S(2)—O(4)	112.0(3)
O(2W)—Ru(1)—P(1)	94.31(10)	C(6)—P(2)—C(29)	103.0(2)	O(5)—S(2)—C(42)	108.4(3)
O(1W)—Ru(1)—P(1)	173.25(10)	C(23)—P(2)—C(29)	99.9(2)	O(6)—S(2)—C(42)	106.7(3)
O(4)—Ru(1)—P(2)	88.47(10)	C(6)—P(2)—Ru(1)	126.15(15)	O(4)—S(2)—C(42)	103.6(2)
O(1)—Ru(1)—P(2)	98.74(10)	C(23)—P(2)—Ru(1)	114.55(16)	S(1)—O(1)—Ru(1)	124.65(19)
O(2W)—Ru(1)—P(2)	167.28(10)	C(29)—P(2)—Ru(1)	110.85(16)	S(2)—O(4)—Ru(1)	126.9(2)
O(1W)—Ru(1)—P(2)	88.84(10)	O(3)—S(1)—O(2)	114.3(2)		

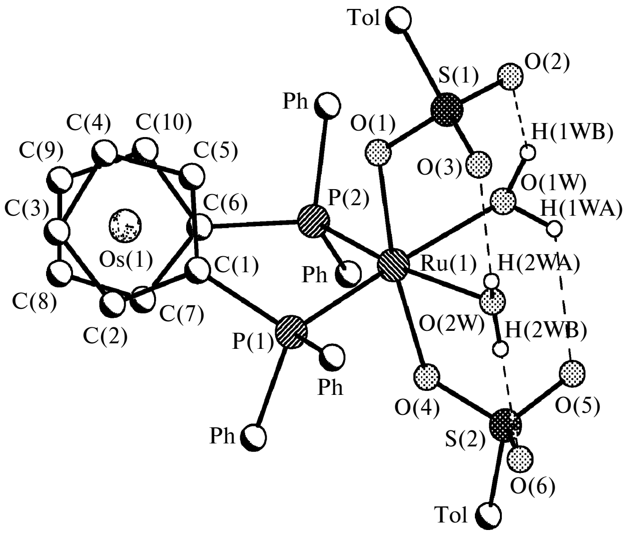
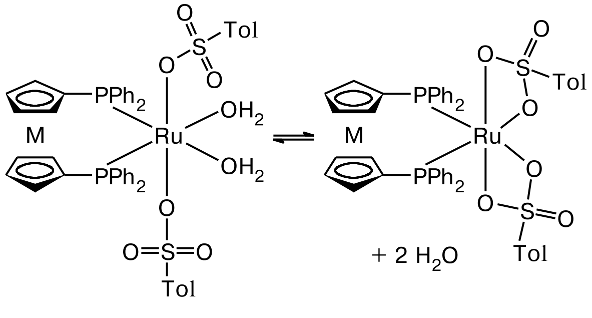


Fig. 1. Overall view of complex **3**. The phenyl and tolyl rings are omitted.

The phosphorus atoms of diphosphine are in *cis* positions; the P(1)—Ru(1)—P(2) angle is 97.84(5)°. There are two H_2O molecules in *trans* positions with respect to the phosphorus atoms. Two tosylate anions are κ^1-coordinated to the ruthenium atom and occupy the apical positions. Two oxygen atoms of the tosylate residues are linked to the water molecules by hydrogen bonds (O...O, 2.698(5)—2.949(5) Å).

Attempts to introduce the second diphosphine molecule by replacing the tosylate anions or water failed. Testing of compounds **1—3** as catalysts for copolymerization of ethylene and carbon monoxide did not show activity of these compounds. Apparently, this behavior can be attributed to the occurrence of the fast equilibrium between the κ^1 and κ^3 bonds of the tosylate anions in solution (Scheme 2) (this fact has been demonstrated[7] for the $Ru(PPh_3)_2(H_2O)(CO)(OTs)_2$ complex), resulting in strengthening of the Ru—OTs bond.

Scheme 2



Experimental

All reactions were carried out under argon using the standard Schlenk technique. The solvents were purified according to

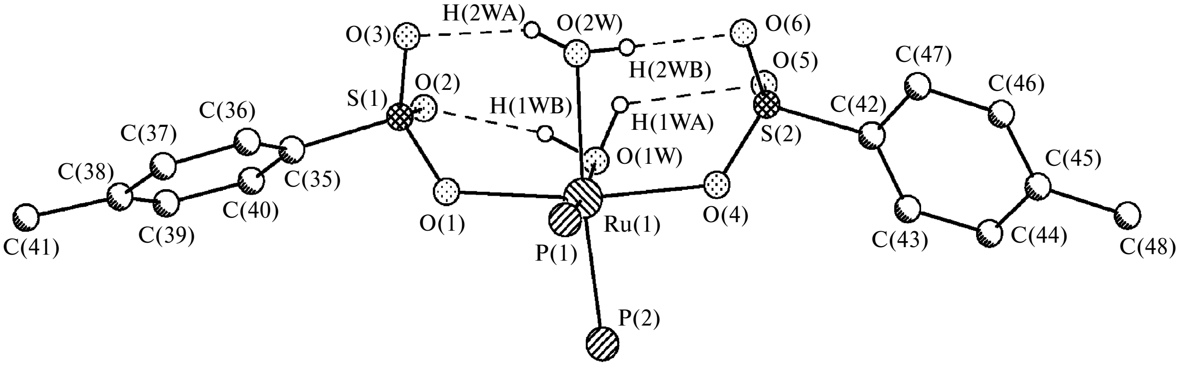


Fig. 2. Coordination polyhedron of the ruthenium atom in complex **3**.

standard procedures. The ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker AMX-400 spectrometer; the chemical shifts are given on the δ scale relative to Me_4Si and 85% H_3PO_4 using $CDCl_3$ as the solvent. The $[Ru(H_2O)_6](OTs)_2$ compound was prepared according to the above-described procedure.[8]

1,1′-Bis(diphenylphosphino)ferrocenylrutheniumdiaquaditosylate (1). The $[Ru(H_2O)_6](OTos)_2$ complex (0.35 g, 0.63 mmol) was added to a solution of 1,1′-bis(diphenylphosphino)ferrocene (0.34 g, 0.62 mmol) in THF (30 mL). The resulting suspension was stirred at 20 °C for 20 h. The resulting orange-brown solution was concentrated *in vacuo* to dryness. The residue was extracted with benzene and filtered. The benzene filtrate was concentrated to 3 mL and allowed to stand for 2 h for crystallization. The yellow precipitate that formed was filtered off, washed with a minimum amount of benzene, and dried *in vacuo*. The yield was 0.35 g (57%). Found (%): C, 55.49; H, 4.85. $C_{48}H_{46}FeO_8P_2RuS_2$. Calculated (%): C, 55.76; H, 4.48. ^{1}H NMR, δ: 2.36 (s, 6 H, 2 Me, OTs); 4.18 and 4.26 (both s, 4 H each, Cp); 7.08 (d, 4 H, OTs, J = 2.0 Hz); 7.27 (m, 8 H, H_m, Ph); 7.29 (d, 4 H, OTs, J = 2.0 Hz); 7.34 (m, 4 H, H_p, Ph); 7.57 (m, 8 H, H_o, Ph). ^{31}P NMR, δ: 58.12 (s). ^{13}C NMR, δ: 21.33 (s, Me, OTs); 72.46 and 75.58 (both s, CH, Cp); 78.82 (t, C, Cp, $J_{C,P}$ = 28.3 Hz); 125.83 (s, CH, OTs); 127.75 (t, *m*-CH, Ph, $J_{C,P}$ = 4.8 Hz); 128.88 (s, CH, OTs); 129.84 (s, *p*-CH, Ph); 134.45 (t, *o*-CH, Ph, $J_{C,P}$ = 4.8 Hz); 135.32 (t, CP, $J_{C,P}$ = 27.5 Hz); 139.50 and 141.82 (both s, C, OTs).

1,1′-Bis(diphenylphosphino)ruthenocenylrutheniumdiaquaditosylate (2) was prepared analogously to compound **1** from 1,1′-bis(diphenylphosphino)ruthenocene (0.36 g, 0.60 mmol) and $[Ru(H_2O)_6](OTs)_2$ (0.33 g, 0.60 mmol). The yield was 0.23 g (37%). Found (%): C, 52.95; H, 4.02. $C_{48}H_{46}O_8P_2Ru_2S_2$. Calculated (%): C, 53.43; H, 4.30. ^{1}H NMR, δ: 2.36 (s, 6 H, 2 Me, OTs); 4.61 and 4.65 (both s, 4 H each, Cp); 7.08 (d, 4 H, OTs, J = 2.0 Hz); 7.22 (m, 8 H, H_m, Ph); 7.29 (d, 4 H, OTs, J = 2.0 Hz); 7.34 (m, 4 H, H_p, Ph); 7.58 (m, 8 H, H_o, Ph). ^{31}P NMR, δ: 54.74 (s). ^{13}C NMR, δ: 21.33 (s, Me, OTs); 75.73 and 77.87 (both s, CH, Cp); 82.56 (t, C, Cp, $J_{C,P}$ = 21.6 Hz); 125.84 (s, CH, OTs); 127.75 (t, *m*-CH, Ph, $J_{C,P}$ = 4.6 Hz); 128.87 (s, CH, OTs); 129.94 (s, *p*-CH, Ph); 134.39 (t, *o*-CH, Ph, $J_{C,P}$ = 4.6 Hz); 134.97 (t, CP, $J_{C,P}$ = 20.6 Hz); 139.41 and 141.84 (both s, C, OTs).

1,1′-Bis(diphenylphosphino)osmocenylrutheniumdiaquaditosylate (3) was prepared analogously to compound **1** from 1,1′-bis(diphenylphosphino)osmocene (0.28 g, 0.4 mmol) and $[Ru(H_2O)_6](OTs)_2$ (0.22 g, 0.40 mmol). The yield was 0.27 g (60%). Found (%): C, 49.40; H, 4.14; Os, 16.09. $C_{48}H_{46}O_8OsP_2RuS_2$. Calculated (%): C, 49.35; H, 3.97; Os, 16.28. ^{1}H NMR, δ: 2.36 (s, 6 H, 2 Me, OTs); 4.81 and 4.87 (both s, 4 H each, Cp); 7.08 (d, 4 H, OTs, J = 2.0 Hz); 7.22 (m, 8 H, H_m, Ph); 7.28 (d, 4 H, OTs, J = 2.0 Hz); 7.34 (m, 4 H, H_p, Ph); 7.59 (m, 8 H, H_o, Ph). ^{31}P NMR, δ: 58.13 (s). ^{13}C NMR, δ: 21.33 (s, Me, OTs); 69.46 and 71.43 (both s, CH, Cp); 75.43 (t, C, Cp, $J_{C,P}$ = 27.5 Hz); 125.85 (s, CH, OTs); 127.80 (t, *m*-CH, Ph, $J_{C,P}$ = 4.4 Hz); 128.88 (s, CH, OTs); 129.96 (s, *p*-CH, Ph); 134.45 (t, *o*-CH, Ph, $J_{C,P}$ = 4.6 Hz); 135.10 (t, CP, $J_{C,P}$ = 22.0 Hz); 139.42 and 141.85 (both s, C, OTs).

X-ray diffraction data for compound **3** ($C_{48}H_{46}O_8OsP_2RuS_2 \cdot H_2O$) were collected at 120 K on an automated three-circle Smart CCD 1000K diffractometer (Mo-Kα radiation, graphite monochromator, ω-scanning technique, $2\theta_{max} \le 58°$). Crystals at 120 K are monoclinic, a = 12.130(2) Å, b = 22.073(4) Å, c = 17.372(3) Å, β = 102.003(3)°, V = 4549.8(13) Å^3, d_{calc} = 1.732 g cm^{-3}, M = 1186.19, F(000) = 2360, μ = 33.41 cm^{-1}, Z = 4 (Z' = 1), space group $P2_1/n$. Of a total of 49674 measured reflections, 11906 independent reflections were used in calculations and refinement. A semiempirical absorption correction was applied based on equivalent reflections using the SADABS program.[9] The structure was solved by direct methods and refined anisotropically by the full-matrix least-squares method against F^2_{hkl}. Analysis of difference Fourier maps demonstrated that the water solvate molecule is disordered over two positions. The coordinates of the hydrogen atoms were calculated geometrically, whereas the H atoms of the disordered water molecule were not located. The final R factors were as follows: R = 0.0457 based on 8637 reflections with $I > 2\sigma(I)$, wR_2 = 0.0916, and GOF = 1.148 based on all reflections. All calculations were carried out using the SHELXTL 5.10 program package.[10] The atomic coordinates were deposited with the Cambridge Structural Database.

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