Orthometalation of Tris(3-sodium sulfonatophenyl)phosphine with Dirhodium(II) Acetate

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Tetraacetatodirhodium(II) reacts with tris(3-sodium sulfonatophenyl)phosphine (TPPTS) giving $[Rh_2(\mu\text{-}OOCCH_3)_3\{\mu\text{-}(3\text{-}NaO_3SC_6H_3)P(C_6H_4SO_3Na\text{-}3)_2\}(HOOCCH_3)]\cdot 6H_2O$ (**1**) and $[Rh_2(\mu\text{-}OOCCH_3)_2\{\mu\text{-}(3\text{-}NaO_3SC_6H_3)P(C_6H_4SO_3Na\text{-}3)_2\}_2(HOOCCH_3)]\cdot 12H_2O$ (**2**). Their structures and properties have been studied by electronic, IR, and $^{31}P\{^1H\}$, ^1H, $^1H\{^{31}P\}$, and $^{13}C\{^1H\}$ NMR spectroscopies. In compound **1**, one of the acetate bridges is replaced by a phosphine ligand, orthometalated via the C^2 carbon atom of the phenyl ring. One axial site of the Rh_2^{4+} core is occupied by a sulfonato group of the metalated ring and another one by a labile molecule of acetic acid. ^1H NMR spectroscopy shows that chemical shifts of the aromatic protons depend on the nature of the axial ligands. Compound **2** contains two orthometalated molecules of TPPTS with a head-to-head structure, and one of these ligands is metalated via the C^2 atom and another one via C^6.

1. Introduction

Dirhodium carboxylates and their derivatives with different ligands are widely investigated[1−20] because of their interesting structure and reactivity,[1−5,9] catalytic properties,[1−4,18] and biological activity.[1−4,6−8] The reactions of orthometalation of aromatic phosphines in binuclear rhodium(II) compounds[1,10−20] have been intensively studied because of growing interest in the problem of activation of the C−H bond. It has been proven that in these reactions phosphine molecules coordinate first at the axial site of the rhodium dimer, migrating further to an equatorial position and forming the Rh−C bond.[11,14,15,17,19,20] The reactions of metalation of triphenylphosphine and other arylphosphines, e.g., halogenophenyl-, methylphenyl-, and trifluoromethylphenylphosphines, can be carried only in organic solvents. However, orthometalation of water-soluble phosphines has, at least to our knowledge, not been investigated up to now. Among them, tris(3-sodium sulfonatophenyl)phosphine (TPPTS) is the subject of a great deal of research interest[21−31] owing to its many applications in biphasic catalysis, including industrial processes,[30,31] because of its extreme solubility in water and insolubility in most organic solvents. Its rather

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S0276-7333(98)00070-3 CCC: $15.00
Publication on Web 07/30/1998

large Tolman's cone angle $\theta = 170°$ [32] is considerably greater than that of triphenylphosphine (PPh_3, $\theta = 145°$) and the same as that of tricyclohexylphosphine (PCy_3). The relatively high steric demands of TPPTS lead to a decreasing reactivity but an increasing selectivity of this phosphine.

The reactions of functionalized phosphines with dirhodium(II) carboxylates, the influence of functional groups in the phosphine ligands on their reactivity, and structures of the resulting complexes are of interest to us. In this paper we report on the reaction of TPPTS with $Rh_2(O_2CCH_3)_4$ in addition to the properties and reactivity of the dirhodium(II) orthometalated complexes.

2. Experimental Section

2.1. Physical Measurements. Infrared spectra (KBr pellet) were recorded on a Bruker IFS 113v, UV−vis on a Beckman DU 7500; ^1H (the residual protons in the solvent used as an internal reference), $^{13}C\{^1H\}$ (dioxane as internal reference), and $^{31}P\{^1H\}$ NMR (85% H_3PO_4 as an external reference) spectra were recorded on a Bruker AMX 300. The amount of rhodium and sodium was determined using ICP-AES method on an ARL 3410.

2.2. Preparation of Complexes. Complex $Rh_2(OOCCH_3)_4$[33] and 1,3,5-triaza-7-phosphatricyclo[3.3.1.1^{3,7}]decane (tpa)[34] were prepared according to the literature method. All solvents were deaerated prior to use. All operations were performed under a dinitrogen atmosphere using standard Schlenk-line techniques.

$P(C_6H_4$-3-$SO_3Na)_3$(TPPTS). This was prepared by a modified method of Herrmann.[23] 1.163 g of $B(OH)_3$ (62.318 mmol) was dissolved in 9 cm^3 of 30% oleum. The excess of SO_3 was evaporated under vacuum, and the mixture was deaerated and cooled to 0 °C. Then 1.011 g (3.854 mmol) of triphenylphosphine (TPP) was added. TPP was dissolved, and then 6 cm^3 of oleum was added. The reaction mixture was stirred at 50 °C for 1 week. After cooling, 50 cm^3 of cold water was cautiously added and the solution was neutralized with 33 g of NaOH in 100 cm^3 of water. The water was removed by vacuum evaporation, and the product (TPPTS) was extracted 2 times with 100 cm^3 of hot methanol. The combined extracts were evaporated to one-fourth of the initial volume, and the TPPTS was precipitated with 400 mL of acetone and filtered. Yield: 1.346 g, 79%.

$[Rh_2(\mu$-$OOCCH_3)_3\{\mu$-(3-$NaO_3SC_6H_3)P(C_6H_4SO_3Na$-3)$_2\}$-$(HOOCCH_3)]\cdot 6H_2O$ (1). A suspension of $[Rh_2(OOCH_3)_4]$ (0.117 g, 0.265 mmol) and TPPTS (0.152 g, 0.266 mmol) in acetic acid (22 cm^3) and acetic anhydride (6 cm^3) was refluxed with stirring for 5 h. The initial orange color of the suspension changed to a deep green solution. The solvent was evaporated under vacuum to one-fourth of the initial volume. Precipitation of the product at this concentration proceeds slowly, but this procedure gives pure compound **1**. The pale green product precipitated after 5 days was filtered and recrystallized from 5 cm^3 of acetic acid. Yield: 0.1541 g, 52%. Anal. Calcd for $C_{26}H_{36}O_{23}PS_3Rh_2Na_3$: C, 27.92; H, 3.24; Rh, 18.40; Na, 6.17. Found: C, 27.58; H, 3.24; Rh, 18.77; Na, 6.53.

$[Rh_2(\mu$-$OOCCH_3)_2\{\mu$-(3-$NaO_3SC_6H_3)P(C_6H_4SO_3Na$-3)$_2\}_2$-$(HOOCCH_3)]\cdot 12H_2O$ (2). A suspension of $[Rh_2(OOCH_3)_4]$ (0.042 g, 0.094 mmol) and TPPTS (0.113 g, 0.197 mmol) in a mixture of 10 cm^3 of acetic acid and 2 cm^3 of acetic anhydride was heated at reflux with stirring for 5 h. The initial orange color of the suspension changed to a deep violet solution containing a pale pink solid. The solvent was evaporated under vacuum to one-half of the initial volume. Pale pink solid was filtered and washed with cold acetic acid. Yield: 0.0636 g, 39 %. Anal. Calcd for $C_{42}H_{56}O_{36}P_2S_6Rh_2Na_6$: C, 29.08; H, 3.25; Rh, 11.86; Na, 7.95. Found: C, 28.65; H, 3.18; Rh, 12.27; Na, 7.56.

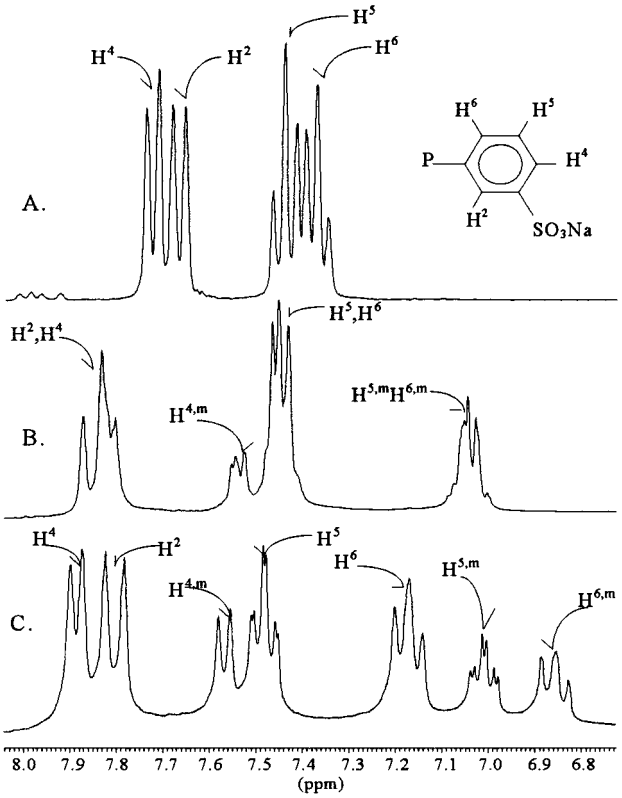

Figure 1. Comparison of ^1H NMR spectra of (A) TPPTS, (B) **1**, and (C) **1** + tpa in D_2O in aromatic region with the numbering scheme (m-orthometalated ring).

3. Results and Discussion

Complexes **1** and **2** are air stable, readily soluble in water, DMSO, and DMF, and slightly soluble in methanol and ethanol. Complex **1**, in contrast to compound **2**, is soluble in glacial acetic acid.

3.1. NMR Spectra. The ^1H NMR spectrum of TPPTS in D_2O (Figure 1A and Table 1) is completely assigned on the basis of relative intensities and comparison with $^1H\{^{31}P\}$ NMR. It consists of two doublets and two triplets assigned to H^4 ($\delta = 7.73$ ppm, d), H^2 ($\delta = 7.67$ ppm, d), H^5 ($\delta = 7.44$ ppm, t), and H^6 ($\delta = 7.37$ ppm, t). The chemical shift of H^4 is higher than that of H^2. This differs from the spectrum of TPPTS in MTW (CD_3OD:THF-d_8:D_2O = 5:3:2)[21] and indicates that the ^1H chemical shifts of TPPTS are relatively sensitive to the nature of the solvent. In DMSO-d_6 (Table 1), the H^2 and H^4 protons have almost the same chemical shifts, resulting in one broad doublet. This signal and the signal of H^6 are shifted to higher fields in comparison with the spectrum of TPPTS in water. Only the chemical shift of H^5 does not change. The largest changes of chemical shifts were observed for H^2 and H^4.

The ^{31}P NMR chemical shifts of the 1:1 and 1:2 adducts of $Rh_2(OAc)_4$ with TPPTS prepared in situ (Table 1) are −39.0 and −16.5 ppm, respectively. The values of $\Delta\delta$ (^{31}P) ($\delta_{complex} - \delta_{phosphine}$) are similar to

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Table 1. NMR Spectra of TPPTS and Its Adducts with Dirhodium Tetraacetate

compound	NMR	δ [ppm], J [Hz]
TPPTS in D_2O	$^{31}P\{^1H\}$	−3.4 (s)
	^1H	H^4: 7.73 (d, 1H), $^3J(H^4-H^5) = 7.7$
		H^2: 7.67 (d, 1H), $^3J\ (H^2-P) = 8.1$
		H^5: 7.44 (t, 1H), $^3J(H^5-H^6) = 7.7$
		H^6: 7.37 (t, 1H), $^3J(H^6-P) = 7.1$
	$^1H\{^{31}P\}$	H^4: 7.73 (d, 1H), $^3J(H^4-H^5) = 7.6$
		H^2: 7.67 (s, 1H)
		H^5: 7.44 (t, 1H), $^3J(H^5-H^6) = 7.6$
		H^6: 7.37 (d, 1H)
TPPTS in DMSO-d_6	$^{31}P\{^1H\}$	−4.5 (s)
	^1H	H^2,H^4: 7.64 (d, 2H), $^3J(H^4-H^5) = {}^3J(H^2-P) = 8.4$
		H^5: 7.39 (t, 1H), $^3J(H^5-H^6) = 7.5$
		H^6: = 7.13 (t, 1H), $^3J(H^6-P) = 7.1$
	$^1H\{^{31}P\}$	H^2,H^4: 7.63 (br s, 2H)
		H^5: 7.38 (t, 1H), $^3J(H^5-H^6) = 7.8$
		H^6: 7.13 (d, 1H)
$Rh_2(OAc)_4$ + 1TPPTS in D_2O	$^{31}P\{^1H\}$	−39.0 (dd), $^1J(Rh-P) = 103$, $^2J(Rh-P) = 24$
	^1H	1.72 (s, 12H)−acetato bridges
		H^2: 8.18 (d, 1H), $^3J(H^2-P) = 10.9$
		H^4: 7.89 (d, 1H), $^3J(H^4-H^5) = 7.7$
		H^5,H^6: 7.57(m, 2H)
$Rh_2(OAc)_4$ + 2TPPTS in D_2O	$^{31}P\{^1H\}$	−16.5 (dd), $^1J(Rh-P) = 48$, $^2J(Rh-P) = 38$
	^1H	1.67 (s, 12H)−acetato bridges
		H^2: 8.15 (br s, 2H)
		H^4: 7.89 (d, 1H), $^3J(H^4-H^5) = 7.7$
		H^6: 7.67 (br s, 2H)
		H^5: 7.58 (t, 2H), $^3J(H^5-H^6) = 7.7$

those of the mono- and bisadducts of rhodium carboxylates with other phosphine and phosphite ligands and show a previously reported trans influence across a binuclear rhodium center.[35,36]

The $^{31}P\{^1H\}$ NMR spectrum of **1** in D_2O consists of a doublet of doublets centered at δ = 18.1 ppm with $^1J(Rh-P)$ = 152 Hz and $^2J(Rh-P)$ = 6 Hz. These chemical shift and coupling constant values are typical for orthometalated dirhodium(II) complexes with phosphines.[11−19] The ^1H NMR of **1** revealed the presence of two bridging acetate groups in a cis position (δ = 1.24 ppm, s, 6H) and one acetato ligand in coordination sites trans to the phosphine ligand (δ = 2.19 ppm, s, 3H). The axial acetato ligand resonates at 1.97 ppm (s, 3H).

In compound **1**, one of the ortho protons of the phenyl ring is split off and a Rh−C bond is formed. The process of metalation can take place in two nonequivalent positions: via C^2 or via C^6. Despite many attempts, we have not been able to obtain single crystals suitable for an X-ray analysis. To resolve the problem of position of metalation, we used NMR spectroscopy. The relative intensities of the signals in the aromatic region of the spectrum of **1**, phosphorus decoupling ($^1H\{^{31}P\}$ NMR), and comparison with the ^1H spectra of TPPTS in D_2O allow us to assign all of the signals (Table 2 and Figure 1B) of the four multiplets at 7.78−7.88 (4H), 7.51−7.56 (1H), 7.41−7.51 (4H), and 7.01−7.09 ppm (2H) to H^2 and H^4 of the nonmetalated phenyl rings, H^4 of the metalated ring, H^5 and H^6 of the nonmetalated rings, and H^5 and H^6 of the metalated ring, respectively. The ^1H NMR spectrum of the 1:1 adduct of **1** with 1,3,5-triaza-7-phosphatricyclo[3.3.1.1^{3,7}]decane (tpa), having a very small Tolman's cone angle (102°), prepared in situ, is comprised of seven signals in the aromatic region (Figure 1C). Analysis of the spectrum of the adduct of **1** with tpa allowed us to assign all of the signals in the ^1H NMR spectrum and to prove the structural characteristics of compound **1** (Figure 2). $^{31}P\{^1H\}$ and ^1H NMR spectra implicate that **1** + tpa is an adduct in which the axial molecule of tpa is bound via a phosphorus atom to the rhodium atom Rh^A. One can see, the signal of $H^{2,m}$ in the ^1H NMR of **1** + tpa is missing. This indicates that the molecule of TPPTS is metalated via atom C^2, most likely caused by additional stabilization due to interaction between the rhodium atom and an oxygen atom of the sulfonato group playing role of an axial ligand. Similar results are obtained from analysis the spectrum of the adduct of **1** with TPPTS. Only the 1:1 adduct with the axial molecule of TPPTS bound to Rh_A is formed. Other axial ligands also influence the chemical shifts of the aromatic protons of compound **1**. The influence of an axial ligand on chemical shifts is given in Figure 3. This shows that the chemical shift of H^6 of nonmetalated rings linearly decreases with an increasing field strength of the axial ligand. The $\delta(H^6)$ changes within the range from 7.78 (I^- adduct) to 7.17 ppm (tpa adduct). Changes of chemical shifts for the other protons are much less (0.1−0.2 ppm).

Compound **2** can be prepared by the direct reaction of 1 mol of $Rh_2(OAc)_4$ with 2 mol of TPPTS or the reaction of **1** with an equimolar quantity of TPPTS. The $^{31}P\{^1H\}$ NMR spectrum of **2** in D_2O consists of two doublets of doublets of doublets centered at δ_A = 13.0 ppm ($^1J(Rh-P_A) = 152$ Hz, $^2J(Rh-P_A) = 9$ Hz, $^2J(P_A-P_B) = 43$ Hz) and δ_B = 25.8 ppm ($^1J(Rh-P_B) = 149$ Hz, $^2J(Rh-P_B) = 7$ Hz). The chemical shifts and coupling constants in the $^{31}P\{^1H\}$ NMR spectrum indicate that compound **2** is doubly metalated complex with a head-to-head structure and two molecules of TPPTS in a cis position. The large differences of the chemical shifts of the phosphorus nuclei suggest two different modes of metalation. The differences of the chemical shifts of analogous complexes, e.g., compounds with two molecules of the same phosphine differing in interactions of functional groups as axial ligands,[11] are much less.

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Table 2. NMR Spectra of Complex 1, Its Adducts, and Compound 2

compound	NMR	δ [ppm], J [Hz]
1 in D_2O	$^{31}P\{^1H\}$	18.1 (dd), $^1J(Rh-P) = 152$, $^2J(Rh-P) = 6$
	^1H	1.24 (s, 6H)—bridges cis to the phosphine
		2.19 (s, 3H)—bridge trans to the phosphine
		1.97 (s, 3H)—axial molecule of acetic acid
		H^2 and H^4: 7.78−7.88 (m, 4H)
		$H^{4,m}$: 7.51−7.56 (m, 1H)
		H^5 and H^6: 7.41−7.51 (m, 4H)
		$H^{5,m}$ and $H^{6,m}$: 7.01−7.09 (m, 2H)
	$^{13}C\{^1H\}$	192.2 (s) COO^{cis}, 185.6 (s) COO^{trans}, 177.4 (s) COOH
		$C^{2,m}$: 164.8 (dd), 27.1 and 28.8 ($^1J(Rh-C^{2,m})$ and $^1J(P-C^{2,m})$)
		$C^{3,m}$: 150.6 (d), $^3J(P-C^{3,m}) = 16.3$
		$C^{1,m}$: 144.9 (d), $^1J(P-C^{1,m}) = 69.8$
		C^3: 143.7 (d), $^3J(P-C^3) = 10.2$
		C^5: 136.0 (d), $^3J(P-C^5) = 7.2$
		$C^{5,m}$: 134.7 (s)
		C^1: 131.9 (d), $^1J(P-C^1) = 50.2$
		C^2: 130.6 (d), $^2J(P-C^2) = 12.1$
		C^6: 130.2 (d), $^2J(P-C^6) = 9.5$
		C^4: 128.3 (s)
		$C^{4,m}$: 128.1 (s)
		$C^{6,m}$: 123.4 (d), $^2J(P-C^{6,m}) = 8.9$
		23.1 (s) $CH_3^{cis} + CH_3^{trans}$, 20.8 (s) CH_3^{HOAc}
1 in DMSO-d_6	$^{31}P\{^1H\}$	14.6 (d), $^1J(Rh-P) = 150$
	^1H	1.21 (s, 6H)—bridges cis to the phosphine
		2.10 (s, 3H)—bridge trans to the phosphine
		1.97 (s, 3H)—axial molecule of acetic acid
		H^2: 7.73 (d, 2H), $^3J(H^2-P) = 11.2$
		H^4: 7 65 (dd, 2H), $^3J(H^4-H^5) = 7.6$, $^4J(H^4-H^6) = 1.4$
		H^6: 7.49 (m., 2H)
		H^5: 7.32 (td, 2H), $^3J(H^5-H^4) \approx {}^3J(H^5-H^6) = 7.7$, $^4J(H^5-P) = 2.1$
		$H^{4,m}$: 7.27 (d, 1H), $^3J(H^4-H^5) = 7.6$
		$H^{5,m}$: 6.90 (td, 1H), $^3J(H^5-H^4) \approx {}^3J(H^5-H^6) = 7.6$, $^4J(H^5-P) = 2.6$
		$H^{6,m}$: 6.66 (td, 1H), $^3J(H^6-P) = 8.3$, $^4J(H^4-H^6) = 1.2$
1 + DMSO in D_2O	$^{31}P\{^1H\}$	17.4 (d), $^1J(Rh-P) = 151$
	^1H	1.26 (s, 6H)—bridges cis to the phosphine
		2.21 (s, 3H)—bridge trans to the phosphine
		1.99 (s, 3H)—axial molecule of acetic acid
		H^2: 7.92 (d, 2H), $^3J(H^2-P) = 11.1$
		H^4: 7.84 (dd, 2H), $^3J(H^4-H^5) = 6.7$, $^4J(H^4-H^6)$ 1.4
		H^6: 7.62 (m, 2H)
		H^5: 7.49 (m, 2H)
		$H^{4,m}$: 7.58 (d, 1H), $J(H^4-H^5) = 7.1$
		$H^{5,m}$: 7.11 (td, 1H), $^3J(H^5-H^4) \approx {}^3J(H^5-H^6) = 7.4$, $^4J(H^5-P) = 2.7$
		$H^{6,m}$: 7.03 (t, 1H), $^3J(H^6-P) = 7.6$
1 + TPPTS in D_2O	$^{31}P\{^1H\}$	A: 12.66 (dt), $^1J(Rh_A-P_A) = 144.8$, $^2J(Rh_B-P_A) \approx J(P_A-P_B) = 5.7$
		B: −41.51 (ddd), $^1J(Rh_A-P_B) = 74.8$, $^2J(Rh_B-P_B) = 48.3$
1 + $N(Et)_3$ in D_2O	$^{31}P\{^1H\}$	19.1(dd) $^1J(Rh\text{-}P_A) = 152.6$, $^2J(Rh-P_A) = 6.1$
	^1H	2.20, (s, 3H)—acetato bridge trans to TPPTS
		1.81, (s, 3H)—free acetic acid
		1.25, (s, 6H)—acetato bridges cis to TPPTS
		H^4: 7.83 (m, 2H)
		H^2: 7.87 (d, 2H), $^3J(H^2-P) = 11.6$
		$H^{4,m}$: 7.55 (m, 1H)
		H^5: 7.48 (m, 2H)
		H^6: 7.46 (m, 2H)
		$H^{5,m}$: = 7.08 (m, 1H)
		$H^{6,m}$: 7.07 (m, 1H)
1 + tpa in D_2O	$^{31}P\{^1H\}$	A: 6.23 (ddd), $^1J(Rh-P_A) = 138.2$, $^2J(Rh-P_A) = 4.3$, $^2J(P_A-P_B) = 11.3$
		B: −129.24 (ddd), $^1J(Rh-P_B) = 83.0$, $^2J(Rh-P_B) = 48.9$
	^1H	4.63, (s, 12H)−tpa
		4.08, (d,12H), $^3J(H-P) = 3.2$−tpa
		2.01, (s, 3H)—acetato bridge trans to TPPTS
		1.91, (s, 3H)—free acetic acid
		1.20, (s, 6H)—acetato bridges cis to TPPTS
		H^4: 7.89 (d, 2H), $^3J(H^4-H^5) = 7.8$
		H^2: 7.81 (d, 2H), $^3J(H^2-P) = 12.2$
		$H^{4,m}$: 7.57 (d, 1H), $^3J(H^4-H^5) = 7.6$
		H^5: 7.48 (td, 2H), $^3J(H^5-H^4) \approx {}^3J(H^5-H^6) = 7$ 8, $^4J(H^5-P) = 1.9$
		H^6: 7.17 (t, 2H), $^3J(H^6-P) = 9.1$
		$H^{5,m}$: = 7.01 (td, 1H), $^3J(H^5-H^4) \approx {}^3J(H^5-H^6) = 7.6$, $^4J(H^5-P) = 2.8$
		$H^{6,m}$: 7.17 (t, 1H), $^3J(H^6-P) = 8.4$

Table 2 (Continued)

compound	NMR	δ [ppm], J [Hz]
1 + 25NaI in D_2O	$^{31}P\{^1H\}$	18.4(d), $^1J(Rh-P) = 147.7$
	^1H	1.30 (s, 6H)—bridges cis to the phosphine
		2.27 (s, 3H)—bridge trans to the phosphine
		1.95 (s, 3H)—free molecule of acetic acid
		H^2: 7.93 (d, 2H), $^3J(H^2-P) = 10.9$
		H^4: 7.88 (d, 2H), $^3J(H^4-H^5) = 7.9$
		H^6: 7.78 (t, 2H), $^3J(H^6-P) = 9.18$
		$H^{4,m}$: 7.71 (d, 1H), $^3J(H^4-H^5) = 7.6$
		H^5: 7 53 (td, 2H), $^3J(H^5-H^4) \approx {}^3J(H^5-H^6) = 7.9$, $^4J(H^5-P) = 2.0$
		$H^{5,m}$: 7.10 (td, 1H), $^3J(H^5-H^4) \approx {}^3J(H^5-H^6) = 7.7$, $^4J(H^5-P) = 2.3$
		$H^{6,m}$: 6.66 (t, 1H), $J(H^6-P) = 8.4$
2 in D_2O	$^{31}P\{^1H\}$	A: 13.0 (ddd), $^1J(Rh-P_A) = 152$, $^2J(Rh-P_A) = 9$, $^2J(P_A-P_B) = 43$
		B: 25.8 (ddd), $^1J(Rh-P_B) = 149$, $^2J(Rh-P_B) = 7$
	^1H	1.10 (s, 3H)—bridging acetate
		1.56 (s; 3H)—bridging acetate
		1.97 (s; 3H)—axial molecule of acetic acid
		6.0−8.2 (m, 22H)—aromatic protons
	$^{31}C\{^1H\}$	185.2 (s) and 184.4 (s)—COO and COOH
		$C^{6,m}$: 172.3 (dd), 39.5 and 24.3 ($^1J(Rh-C^{6,m})$ and $^1J(P-C^{6,m})$)
		$C^{2,m}$: 166.3 (dd), 35.4 and 25.7 ($^1J(Rh-C^{2,m})$ and $^1J(P-C^{2,m})$)
		148−121—the rest of aromatic carbon atoms
		24.1 (s) and 23.1 (s) CH_3

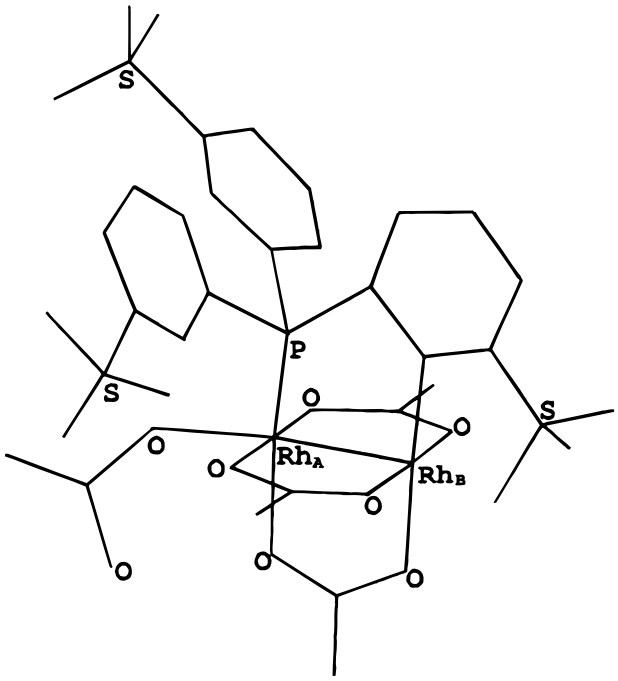
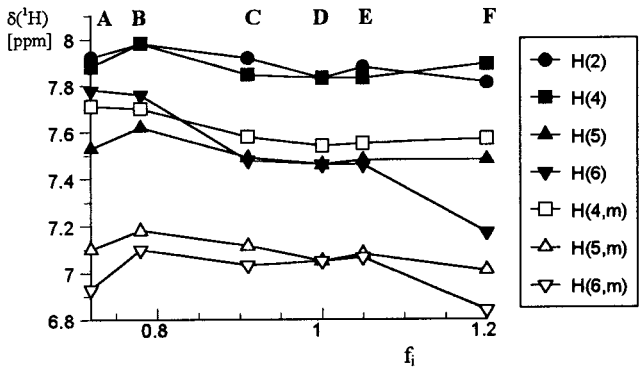


Figure 2. Molecular structure of **1** established by spectroscopic methods.



$$f_i = \frac{10Dq(L_i)}{10Dq(H_2O)}$$

Figure 3. Dependence of chemical shifts of aromatic protons of complex **1** in D_2O solutions on axial ligand field strength: (A) **1** + NaI; (B) **1** + NaCl; (C) **1** + DMSO; (D) **1** in D_2O; (E) **1** + $N(CH_2CH_3)_3$; (F) **1** + tpa.

Thus, one molecule of TPPTS is most likely metalated via C^2 and the second one via C^6 (Figure 4). Our analysis is supported by ^1H NMR of the carboxylate protons. The chemical shifts of the acetate bridges are 1.10 (s; 3H) and 1.56 ppm (s; 3H) and the axial CH_3COOH molecule 1.97 ppm (s; 3H). However, $HOOCH_3$ molecules in complex **1** and **2** are bound rather weakly. They can be completely removed; after prolonged drying, only two signals of the CH_3 groups are observed in the ^1H NMR spectra of both complexes. The complicated proton spectrum of complex **2** in the aromatic region (14 groups of signals) also agrees with the proposed structure presented in Figure 4. One axial site of the rhodium dimer is occupied by a sulfonato group and the second one by a compact ligand, e.g., tpa, DMSO, or I^-, what has been proven by the ^1H and ^{31}P NMR spectra. However, in the case of complex **2**, coordination of the axial ligand is weaker than that in compound **1**. The interaction of the bulky TPPTS ligand with **2** is very weak.

The proposed structures of compounds **1** and **2** are also confirmed by $^{13}C\{^1H\}$ NMR. The assignment of the ^{13}C NMR signals for complex **1** based on $^{13}C-^{31}P$ and $^{13}C-^{103}Rh$ coupling constants found for rhodium−phosphine complexes,[15] the very well-known downfield shift of the carbon bound to the metal,[37] the low intensity of the signals of the quaternary carbon atoms, and $^{13}C-^1H$ COSY NMR as well as $^{13}C\{^1H\}$ NMR spectra of TPPTS[21] and its oxide TPPTSO[21] are given in Table 2.

In complex **2**, all of the carbon atoms of both TPPTS ligands are nonequivalent. In the ^{13}C NMR spectrum of this compound (Figure 5), we have observed 36 signals for the aromatic carbon atoms, 2 signals for the CH_3 groups (24.1 and 23.1 ppm), and 2 signals for the COO groups (185.2 and 184.4 ppm). In the aromatic region it was possible to assign only the two signals of the metalated carbon atoms of the phenyl rings at 172.3 ($C^{6,m}$) and 166.3 ppm ($C^{2,m}$). Thus, these data also indicate that one TPPTS ligand is coordinated via the

Table 3. IR Spectra of Complexes 1 and 2 (KBr Pellet)

	ν [cm^{-1}]					
compound	$\nu_{as}(CO_2)$	$\nu_s(CO_2)$	$\nu_{as}(SO_3)$	$\nu_s(SO_3)$	$\nu_{as}(RhO)$	$\nu_s(RhO)$
$Rh_2(OAc)_4$	1580 (vs)	1443 (vs)			380 (m)	354 (m)
1	1574 (vs)	1426 (s)	1222 (vs)	1038 (vs)	380 (m)	350 (w)
2	1556 (s)	1426 (s)	1202 (vs)	1038 (vs)	not observed	not observed
TPPTS			1206 (vs)	1048 (vs)		

Table 4. UV−vis Spectra of Complexes in H_2O Solution

	λ_{max} [nm] (ϵ [dm^3 mol^{-1} cm^{-1}])		
compound	$\pi^*(Rh_2) \rightarrow \sigma^*(Rh_2)$	$\pi^*(Rh_2) \rightarrow \delta^*(Rh-L_{eq})$	$\sigma(Rh-L_{ax}) \rightarrow \sigma^*(Rh_2)$
$Rh_2(OAc)_4$	588 (230)	446 (95)	220 (10 000)[a]
$Rh_2(OAc)_4$ + TPPTS	480 (1450)	hidden under CT trans	365 (12 500)[b]
1	620 (120)	521 (90)	323 (2690)[c]
1 + TPPTS	587 (150)	494 (190)	325 (18 500)[c]
2	530 (250)	427 (350)	300 (13 100)[c]
2 + TPPTS	533 (220)	429 (320)	282 (36 900)[c]

[a] L = H_2O_{ax}. [b] L = R_3P_{ax}. [c] L = R_3P_{eq}.

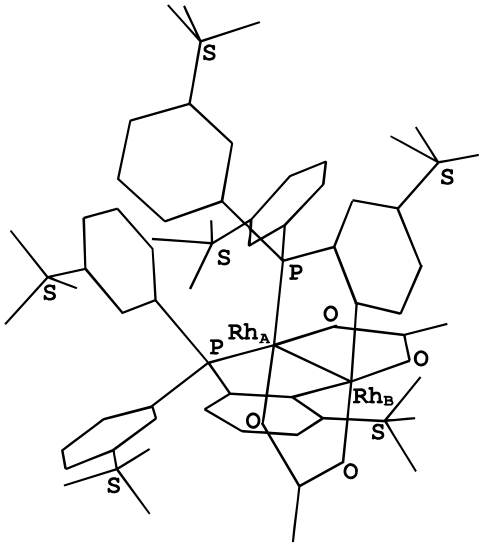


Figure 4. Proposed structure of **2**.

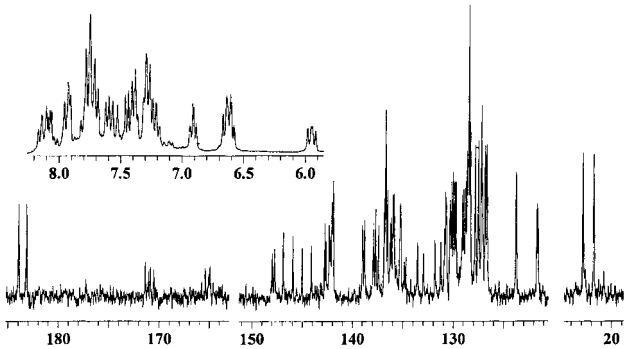


Figure 5. $^{13}C\{^1H\}$ NMR spectrum (lower) and aromatic range of ^1H spectrum (upper) of **2**.

C^2 atom and the other via the C^6 atom. This leads to the unequivalency of the acetato ligands.

3.2. IR UV−vis Spectra. The IR spectra (Table 3) indicate that the acetato bridges are symmetrical, because the differences between symmetrical and asymmetrical stretching vibrations of CO_2 groups are relatively small. The ν(Rh−O) of stretching vibrations for complex **1** are observed almost at the same frequencies as for rhodium acetate.

In the visible region of the electronic spectra (Table 4) of the investigated complexes, two bands are observed. For the monometalated compound **1**, they appear at 620 and 521 nm and are red-shifted by about 30 and 75 nm, respectively, in comparison with rhodium acetate. The first band should be assigned to the transition $\pi^*(Rh_2) \rightarrow \sigma^*(Rh_2)$ and the second one to the transition $\pi^*(Rh_2) \rightarrow \delta^*(Rh-L_{equatorial})$.[5] The bands caused by these transitions in the doubly metalated compound, **2**, are observed at 530 and 427 nm. The strong changes in the energy of the bands in the visible range for both complexes prove that introduction of orthometalated ligands strongly changes the energy of the Rh_2 core orbitals. The first band in the visible spectrum of **1** is blue-shifted by 33 nm after coordination of TPPTS ligand along the Rh−Rh axis (i.e., after formation of the monoadduct). An analogous blue shift was found for the phosphine adduct of rhodium tetraacetate. However, the spectrum of **2** and its mixture with TPPTS in the visible region are almost identical, proving that the adduct of **2** with TPPTS is very weak. This agrees with the conclusions resulting from analysis of the NMR spectra.

Acknowledgment. Financial support of this research by KBN (Grant No. 3 T09A 092 10) is greatly appreciated.

OM9800703