Journal of Organometallic Chemistry 733 (2013) 53–59

Contents lists available at SciVerse ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Unusual stability of reaction intermediates in *ortho*-metalation reactions of dicyclohexylphenylphosphane with dirhodium(II) tetraacetate

Konrad Herbst*, Mercedes Sanaú, Francisco Estevan, M. Angeles Úbeda

Departamento de Química Inorgánica, Facultad de Química, Universidad de Valencia, Dr. Moliner 50, 46100 Burjassot, Valencia, Spain

ARTICLE INFO

Article history:
Received 15 January 2013
Received in revised form
14 February 2013
Accepted 19 February 2013

Keywords:
Rhodium
ortho-Metalation
Acetate
Trifluoroacetate

ABSTRACT

Reaction of dirhodium(II) tetraacetate with 1 molar equivalent of dicyclohexylphenylphosphane afforded the complex $[Rh_2(\mu\text{-}O_2CCH_3)_3\{\mu\text{-}(C_6H_4)PCy_2\}(CH_3COOH)_2]$ (**1**) in which the phosphane ligand is coordinated to the rhodium atoms in a bridging *ortho*-metalated mode. As a second product, $[Rh_2(\mu\text{-}O_2CCH_3)_3\{\mu\text{-}(C_6H_4)PCy_2\}(CH_3COOH)(PhPCy_2)]$ (**2**) was isolated from the same reaction. **2** proved to be unusually stable toward further reaction to a doubly *ortho*-metalated complex which has been accessible in the reaction of dirhodium(II) tetraacetate with other phosphane ligands. However, doubly *ortho*-metalated $[Rh_2(\mu\text{-}O_2CCH_3)_2\{\mu\text{-}(C_6H_4)PCy_2\}_2(CH_3COOH)_2]$ (**4**) was isolated in low yield after a prolonged thermal reaction between dirhodium(II) tetraacetate and 2 equivalents of $PhPCy_2$. Exchange of the bridging acetate ligands in **1** and **4** by trifluoroacetate ligands afforded $[Rh_2(\mu\text{-}O_2CCF_3)_3\{\mu\text{-}(C_6H_4)PCy_2\}(CF_3COOH)_2]$ (**5**) and $[Rh_2(\mu\text{-}O_2CCF_3)_2\{\mu\text{-}(C_6H_4)PCy_2\}_2(CF_3COOH)_2]$ (**7a**). Complex **7a** without axial ligands, $[Rh_2(\mu\text{-}O_2CCF_3)_2\{\mu\text{-}(C_6H_4)PCy_2\}_2]$ (**7b**) was isolated, as well. The crystal structure of complex **5** was determined showing consequences of the bulky cyclohexyl groups on several structural parameters.

1. Introduction

The intramolecular C–H activation of aryl phosphane ligands by dirhodium(II) tetraacetate has been subject of detailed investigations since the discovery of this reaction type in 1984 [1,2]. Formally being an acid–base reaction, a phenyl proton in *ortho* position to the P–C bond protonates a bridging acetate ligand which is subsequently removed from the Rh dimer as a molecule of free acetic acid. The phosphane ligand then adopts a bridging coordination mode to the rhodium atoms with one aryl ring being metalated at one of the *ortho* positions. At maximum two of the bridging acetate ligands in $[Rh(\mu\text{-}O_2CCH_3)_4]$ can be substituted by such *ortho*-metalated phosphane ligands [3]. In terms of a general reaction scheme, *ortho*-metalation at a rhodium(II) dimer is initiated by the coordination of the phosphane ligands in axial position to the rhodium atoms which is possible in solution already at ambient conditions. Rearrangement of the phosphane ligands into equatorial position and C–H activation usually requires thermal reaction conditions (e.g. in mixtures of boiling toluene/acetic acid) [4]. Several reaction intermediates with various triaryl phosphane ligands have been structurally characterized over the last years by the group of Lahuerta et al. [5–10].

Doubly metalated rhodium(II) complexes are inherently chiral when the phosphane ligands adopt a head-to-tail configuration [11]. Substitution of the acetate ligands for chiral carboxylate ligands leads to diasteromers whose separation by column chromatography succeeded in a number of cases [11–13]. The separated diastereomers may be back-transformed to a pair of (now resolved) enantiomers by reaction with a non-chiral carboxylic acid. Doubly *ortho*-metalated rhodium(II) carboxylate complexes are active catalysts in C–H insertion and cyclopropanation reactions of α-diazo ketones [12–17]. The possibility of applying chiral catalysts in these types of reactions has in recent years increased the interest in this type of enantiopure rhodium(II) complexes, since the product enantioselectivity can be effectively controlled by the electronic and steric properties of the organic substituents at the carboxylate and phosphane ligands [18,19]. The experimental results were also supported by quantum chemical density functional theory calculations on the electronic properties of the ligands [20].

The reaction pathways of many phosphane ligands toward dirhodium(II) tetraacetate have been systematically investigated. In some cases these studies delivered unexpected results, the latest example being the ring rearrangement of a thiophene ring in a tris(2-thienyl)phosphane ligand coordinated to the Rh dimer [21]. A previous example is the rearrangement of an *ortho*-metalated

* Corresponding author. Present address: Haldor Topsøe A/S, Nymøllevej 55, DK-2800 Lyngby, Denmark. Tel.: +45 22496679.
E-mail address: knh@topsoe.dk (K. Herbst).

0022-328X/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jorganchem.2013.02.030

methyldiphenylphosphane ligand by reaction of the complex with two equivalents of PPh_3 resulting in the metalation of the methyl group [9].

In the present study, we have investigated the reaction of another mixed alkyl–aryl phosphane, dicyclohexylphenylphosphane, toward dirhodium(II) tetraacetate. Two factors, the bulkiness of the cyclohexyl groups and the increase of the basicity at the phosphorus atom induced by the cyclohexyl groups, make $PhPCy_2$ an interesting ligand for studies of the coordinative behavior toward dirhodium(II) acetate.

2. Experimental

2.1. General

All preparations were carried out under an atmosphere of dry nitrogen using Schlenk techniques. Solvents were dried and distilled from standard drying agents prior to use. Solvent mixtures are on volume/volume basis. ^1H, $^{13}C\{^1H\}$, $^{19}F\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AC-300 FT spectrometer as $CDCl_3$ solutions. Chemical shifts are reported in ppm, using TMS (^1H, ^{13}C), $CFCl_3$ (^{19}F) and 85% H_3PO_4 (^{31}P) as references. The coupling constants (J) are in hertz (Hz). UV/vis spectra were recorded on a Varian Cary 300 Bio UV/visible spectrophotometer. Solutions for UV/vis spectroscopy were prepared by dissolution of a weighted amount of the complex (10–20 mg) in 50 ml $CHCl_3$ containing 1% of ethanol with addition of one drop of CH_3COOH or CF_3COOH. X-ray structure determination was carried out on a Bruker–Nonius Kappa CCD diffractometer (Mo Kα radiation, $\lambda = 0.71073$ Å). Chemical analyzes were performed at the Centro Microanálisis Elemental, Universidad Complutense de Madrid, Spain.

$[Rh_2(\mu\text{-}O_2CCH_3)_4(CH_3OH)_2]$ was purchased from Pressure Chemical Co. $PhPCy_2$ was purchased from Aldrich.

2.2. Synthesis of $[Rh_2(\mu\text{-}O_2CCH_3)_3\{\mu\text{-}(C_6H_4)PCy_2\}(CH_3COOH)_2]$ (**1**)

$[Rh_2(\mu\text{-}O_2CCH_3)_4(CH_3OH)_2]$ (506 mg, 1.00 mmol) and $PhPCy_2$ (275 mg, 1.00 mmol) in a mixture of toluene:acetic acid (3:1, 30 ml) were heated to reflux for 2 h. After evaporating the solvents to dryness, the crude product was dissolved in CH_2Cl_2 (4 ml) for chromatographic purification on silica-gel (hexane, 40 × 3 cm). Elution with hexane:CH_2Cl_2:CH_3COOH (40:20:1 by volume) afforded as first fraction a small magenta colored band of $[Rh_2(\mu\text{-}O_2CCH_3)_3\{\mu\text{-}(C_6H_4)PCy_2\}(CH_3COOH)(PhPCy_2)]$ (**2**), then a major blue band of **1**. After evaporation of the solvents, a dark blue powder was obtained. Yield: 545 mg (0.70 mmol, 70%). ^1H NMR ($CDCl_3$, δ/ppm): 0.83–2.21 (m, 22H, C_6H_{11}); 1.68 (s, 6H, CH_3); 2.25 (s, 6H, CH_3); 2.36 (s, 3H, CH_3); 6.95 (m, 2H, C_6H_4); 7.17 (m, 1H, C_6H_4); 8.61 (m, 1H, C_6H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ/ppm): 21.6 (s, CH_3); 22.8 (s, CH_3); 24.0 (s, CH_3); 26.3–37.6 (cyclohexyl carbons); 121.3–143.1 (aromatics); 161.1 (dd, ^1J(RhC) = 33 Hz, ^2J(PC) = 20 Hz, metalated C); 178.8 (s, COO); 182.2 (d, J = 2.1 Hz, COO *trans* P); 189.6 (s, COO). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ/ppm): 22.2 (dd, ^1J(RhP) = 151 Hz, ^2J(RhP) = 6 Hz). UV/vis ($CHCl_3$, λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})): 243 (10,000); 276 (9900); 381sh (300); 565 (190); 626 (190). Anal. Calcd. for $C_{28}H_{43}O_{10}PRh_2$ (776.43): C, 43.31; H, 5.58. Found: C, 43.81; H, 5.46.

2.3. Synthesis of $[Rh_2(\mu\text{-}O_2CCH_3)_3\{\mu\text{-}(C_6H_4)PCy_2\}(CH_3COOH)(PhPCy_2)]$ (**2**)

A solution of $PhPCy_2$ (30 mg, 0.11 mmol) in $CHCl_3$ (2 ml) was added to a solution of **1** (85 mg, 0.11 mmol) in $CHCl_3$ (20 ml). The color of the solution changed immediately to magenta. After stirring for 30 min, the solvent was evaporated in a vacuum. The oily residue can be crystallized from a mixture of CH_2Cl_2/hexane. Yield: 110 mg (0.11 mmol, 96%) ^1H NMR ($CDCl_3$, δ/ppm): 0.80–1.97 (m, 44H, C_6H_{11}); 1.65 (s, 6H, CH_3); 2.09 (s, 3H, CH_3); 2.25 (s, 3H, CH_3); 6.35 (t, J = 7.5 Hz, 1H, C_6H_4); 6.63 (t, J = 7.2 Hz, 1H, C_6H_4); 6.85 (m, 1H, C_6H_4); 7.32–7.48 (m, 4H, C_6H_4 + C_6H_5); 7.69 (t, J = 7.4 Hz, 2H, C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ/ppm): 14.2 (s, CH_3); 20.8 (s, CH_3); 22.7 (s, CH_3); 23.8–37.0 (cyclohexyl carbons); 119.0–147.5 (aromatics); 157.1 (dd, ^1J(RhC) = 32 Hz, ^2J(PC) = 20 Hz, metalated C); 176.0 (s, COO); 180.5 (d, J = 2.1 Hz, COO); 188.0 (s, COO). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ/ppm): −16.8 (ddd, ^1J(RhP) = 111 Hz, ^2J(RhP) = 33 Hz, ^3J(PP') = 12 Hz, axial P); 28.3 (ddd, ^1J(RhP) = 155 Hz, ^2J(RhP) = 2 Hz). UV/vis ($CHCl_3$, λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})): 258 (9700); 303sh (9000); 338 (16,000); 523 (1200). Anal. Calcd. for $C_{44}H_{66}O_8P_2Rh_2\cdot\frac{1}{2}C_6H_{14}$ (1033.85): C, 54.60; H, 7.12. Found: C, 54.36; H, 7.32.

2.4. Synthesis of $[Rh_2(\mu\text{-}O_2CCH_3)_2(\eta\text{-}O_2CCH_3)\{\mu\text{-}(C_6H_4)PCy_2\}(CH_3COOH)(PhPCy_2)]$ (**3**)

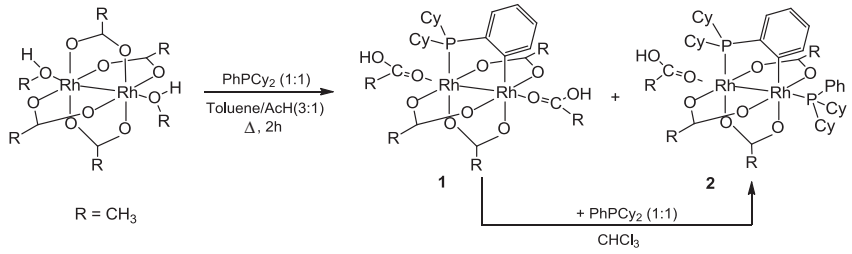
A solution of **2** (40 mg, 0.04 mmol) in $CDCl_3$ (0.7 ml) was irradiated by a Hg–quartz lamp for 1 h. The color of the solution slowly changed to dark-brown. The reaction product was identified by NMR spectroscopy in solution. ^1H NMR ($CDCl_3$, δ/ppm): 0.7–2.3 (m, 44H, C_6H_{11}); 1.24 (s, 3H, CH_3); 2.02 (s, 3H, CH_3); 2.11 (s, 6H, CH_3); 6.68 (t, J = 7.3 Hz, 1H, C_6H_4); 6.78 (t, J = 7.5 Hz, 1H, C_6H_4); 6.94 (t, J = 7.4 Hz, 1H, C_6H_4); 7.15–7.57 (m, 3H, C_6H_5); 7.60–7.80 (m, 2H, C_6H_5); 8.02 (m, 1H, C_6H_4). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ/ppm): 18.7 (dd, ^1J(RhP) = 141 Hz, ^2J(RhP) = 9 Hz), 36.1 (dd, ^1J(RhP) = 178 Hz, ^2J(RhP) = 4 Hz).

2.5. Synthesis of $[Rh_2(\mu\text{-}O_2CCH_3)_2\{\mu\text{-}(C_6H_4)PCy_2\}_2(CH_3COOH)_2]$ (**4**)

$[Rh_2(\mu\text{-}O_2CCH_3)_4(CH_3OH)_2]$ (170 mg, 0.34 mmol) and $PhPCy_2$ (234 mg, 0.85 mmol) in a mixture of toluene:acetic acid (3:1, 30 ml) were heated to reflux for 24 h. After evaporating the solvents to dryness, the crude product was dissolved in CH_2Cl_2 (4 ml) for chromatographic purification on silica-gel (hexane, 40 × 3 cm). Elution with hexane:CH_2Cl_2:acetic acid (100:100:1) afforded a violet band (without acetic acid: green band) which was collected. Evaporation of the solvents in a vacuum resulted in a violet powder. Yield: 135 mg (0.14 mmol, 41%). ^1H NMR ($CDCl_3$, δ/ppm): 0.44–1.97 (m, 44H, C_6H_{11}); 2.03 (s, 6H, CH_3); 2.15 (s, 6H, CH_3); 6.69 (t, J = 7.1 Hz, 2H, C_6H_4); 6.79 (t, J = 7.2 Hz, 2H, C_6H_4); 6.95 (t, J = 7.1 Hz, 2H, C_6H_4); 7.97 (m, 2H, C_6H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ/ppm): 22.1 (s, CH_3); 24.2 (s, CH_3); 35.9–37.1 (cyclohexyl carbons); 120.2–146.0 (aromatics); 163.6 (m, metalated C); 178.6 (s, COO); 181.4 (s, COO). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ/ppm): 18.7 (AA'XX' system). UV/vis ($CHCl_3$, λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})): 243 (20,400); 295 (13,800); 385 (490); 564 (330). Anal. Calcd. for $C_{44}H_{66}O_8P_2Rh_2\cdot C_6H_{14}$ (1076.94): C, 55.76; H, 7.49. Found: C, 55.77; H, 6.91.

2.6. Synthesis of $[Rh_2(\mu\text{-}O_2CCF_3)_3\{\mu\text{-}(C_6H_4)PCy_2\}(CF_3COOH)_2]$ (**5**)

CF_3COOH (2 ml) was added to a solution of **1** (100 mg, 0.13 mmol) in $CHCl_3$ (20 ml). After 24 h of stirring, the solvents were evaporated in a vacuum. The green solid was re-dissolved in $CHCl_3$:CF_3COOH (10:1) and the process repeated. Yield: 132 mg (0.13 mmol, 98%). ^1H NMR ($CDCl_3$, δ/ppm): 0.80–2.48 (m, 22H, C_6H_{11}); 7.02–7.16 (m, 2H, C_6H_4); 7.29 (t, J = 5.9 Hz, 1H, C_6H_4); 8.42 (m, 1H, C_6H_4); 8.83 (s, br, 2H, COOH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ/ppm): 25.8–37.8 (cyclohexyl carbons); 111.3 (q, ^1J(CF) = 290 Hz, CF_3); 114.3 (q, ^1J(CF) = 285 Hz, CF_3); 115.2 (q, ^1J(CF) = 282 Hz, CF_3); 123.2–141.8 (aromatics); 153.1 (dd, ^1J(RhC) = 31 Hz, ^2J(PC) = 17 Hz,



Scheme 1. Synthesis of **1** and **2**.

metalated C); 163.5 (q, ^2J(CF) = 43 Hz, COO); 168.0 (q, ^2J(CF) = 40 Hz, COO *trans* P); 174.6 (q, ^2J(CF) = 40 Hz, COO); $^{19}F\{^1H\}$ NMR ($CDCl_3$, δ/ppm): −75.7 (s, 6F); −75.3 (s, 3F); −74.9 (6F). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ/ppm): 22.7 (dd, ^1J(RhP) = 142 Hz, ^2J(RhP) = 5 Hz). UV/vis ($CHCl_3$, λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})): 245 (12,800); 276sh (8300); 388sh (370); 576 (190); 647 (160). Anal. Calcd. for $C_{28}H_{28}F_{15}O_{10}PRh_2$ (1046.28): C, 32.14; H, 2.70. Found C, 32.39; H, 2.78.

2.7. Synthesis of $[Rh_2(\mu\text{-}O_2CCF_3)_3\{\mu\text{-}(C_6H_4)PCy_2\}(CF_3COOH)(PhPCy_2)]$ (**6**)

The same procedure as for the synthesis of **2** was employed using **5** (115 mg, 0.11 mmol) and $PhPCy_2$ (30 mg, 0.11 mmol). Yield: 130 mg (0.11 mmol, 98%). ^1H NMR ($CDCl_3$, δ/ppm): 0.80–2.40 (m, 44H, C_6H_{11}); 6.44 (t, J = 8.2 Hz, 1H, C_6H_4); 6.74 (t, J = 7.1 Hz, 1H, C_6H_4); 6.90 (m, 1H, C_6H_4); 7.35–7.52 (m, 4H, C_6H_5 + C_6H_4); 7.63 (t, J = 8.2 Hz, 2H, C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ/ppm): 25.6–37.5 (cyclohexyl carbons); 111.1 (q, ^1J(CF) = 288 Hz, CF_3); 114.7 (q, ^1J(CF) = 288 Hz, CF_3); 115.4 (q, ^1J(CF) = 282 Hz, CF_3); 121.3–148.0 (aromatics); 150.0 (dd, ^1J(RhC) = 31 Hz, ^2J(PC) = 18 Hz, metalated C); 160.2 (q, ^2J(CF) = 40 Hz, COO); 166.9 (q, ^2J(CF) = 39 Hz, COO); 173.3 (q, ^2J(CF) = 39 Hz, COO). $^{19}F\{^1H\}$ NMR ($CDCl_3$, δ/ppm): −76.0 (s, br, 3F); −75.0 (s, 6F); −74.9 (s, 3F). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ/ppm): −14.4 (ddd, ^1J(RhP) = 113 Hz, ^2J(RhP) = 25 Hz, ^3J(PP') = 10 Hz, axial P); 26.1 (dd, ^1J(RhP) = 149 Hz). UV/vis ($CHCl_3$, λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})): 243 (13,500); 289 (10,500); 354 (11,800); 526 (1400). Anal. Calcd. for $C_{44}H_{54}F_{12}O_8P_2Rh_2$ (1206.64): C, 43.80; H, 4.51. Found: C, 43.58; H, 4.51.

2.8. Synthesis of $[Rh_2(\mu\text{-}O_2CCF_3)_2\{\mu\text{-}(C_6H_4)PCy_2\}_2(CF_3COOH)_2]$ (**7a**)

CF_3COOH (1 ml) was added to a solution of **4** (50 mg, 0.05 mmol) in $CHCl_3$ (10 ml). After stirring for 1 h, the product was purified by column chromatography on silica-gel (hexane, 20 × 2 cm). Elution with CH_2Cl_2:hexane:CF_3COOH (200:100:1) yielded a green band which was collected and evaporated to dryness. Repeated evaporation of the residue from hexane resulted in crystallization of the product as a green powder. Yield: 53 mg (0.044 mmol, 87%). ^1H NMR ($CDCl_3$, δ/ppm): 0.59–2.05 (m, 44H, C_6H_{11}); 5.45 (s, br, 2H, COOH); 6.77 (m, 2H, C_6H_4); 6.92 (t, J = 7.6 Hz, 2H, C_6H_4); 7.02 (t, J = 7.8 Hz, 2H, C_6H_4); 7.65 (m, 2H, C_6H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ/ppm): 25.5–38.5 (cyclohexyl carbons); 114.4 (q, ^1J(CF) = 286 Hz, CF_3); 114.9 (q, ^1J(CF) = 287 Hz, CF_3); 121.9–146.0 (aromatics); 157.5 (m, metalated C); 161.7 (q, ^2J(CF) = 43 Hz, COO); 167.3 (q, ^2J(CF) = 39 Hz, COO). $^{19}F\{^1H\}$ NMR ($CDCl_3$, δ/ppm): −76.2 (s, 6F); −75.5 (s, 6F). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ/ppm): 18.5 (AA'XX' system). UV/vis ($CHCl_3$, λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})): 255 (15,300); 293 (12,700); 410 (390); 651 (280). Anal. Calcd. for $C_{44}H_{54}F_{12}O_8P_2Rh_2$ (1206.64): C, 43.80; H, 4.51. Found: C, 44.31; H, 4.51.

2.9. Synthesis of $[Rh_2(\mu\text{-}O_2CCF_3)_2\{\mu\text{-}(C_6H_4)PCy_2\}_2]$ (**7b**)

The compound was obtained by heating **7a** at 80 °C for 1 h in a vacuum. ^1H NMR ($CDCl_3$, δ/ppm): 0.52–2.10 (m, 44H, C_6H_{11}); 6.75 (m, 2H, C_6H_4); 6.90 (t, J = 7.2 Hz, 2H, C_6H_4); 7.00 (t, J = 7.2 Hz, 2H, C_6H_4); 7.62 (m, 2H, C_6H_4). $^{19}F\{^1H\}$ NMR ($CDCl_3$, δ/ppm): −75.0 (s). Anal. Calcd. for $C_{40}H_{52}F_6O_4P_2Rh_2$ (978.60): C, 49.09; H, 5.36. Found: C, 49.25; H, 5.68.

2.10. Crystallographic study

The structure was solved by direct methods using the SHELXTL software package [22]. The correct positions for the heavy atoms were deduced from an E-map. Subsequent least-squares refinement and difference Fourier calculations revealed the positions of the remaining non-hydrogen atoms. Hydrogen atoms were placed in geometrically generated positions and refined riding on the atom to which they are attached.

3. Results and discussion

3.1. Syntheses and spectroscopic characterizations

An established procedure for the synthesis of singly and doubly *ortho*-metalated dirhodium(II) phosphane complexes consists of a thermal reaction of dirhodium(II) tetraacetate with one or two equivalents of the phosphane ligand in a boiling mixture of toluene and acetic acid (3:1). These conditions generally lead within 2 h reaction time to a formation of the singly or doubly-metalated complex in high yield, a side product in the synthesis of the singly-metalated complex being small amounts of the doubly-metalated compound. However, employing these conditions in

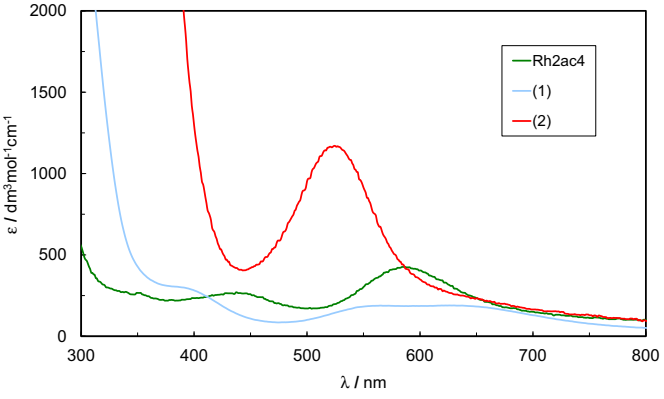
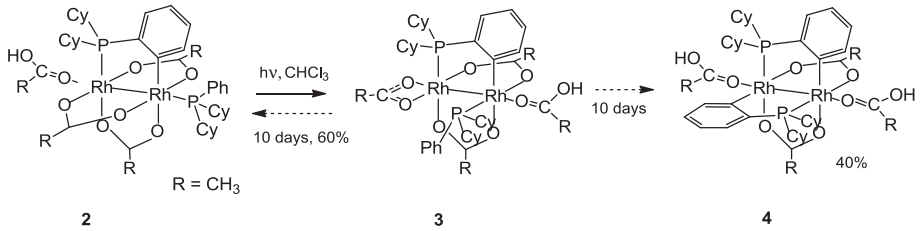


Fig. 1. UV/vis spectra of $[Rh_2(\mu\text{-}O_2CCH_3)_4(CH_3COOH)_2]$, $[Rh_2(\mu\text{-}O_2CCH_3)_3\{\mu\text{-}(C_6H_4)PCy_2\}(CH_3COOH)_2]$ (**1**) and $[Rh_2(\mu\text{-}O_2CCH_3)_3\{\mu\text{-}(C_6H_4)PCy_2\}(CH_3COOH)(PhPCy_2)]$ (**2**) dissolved in $CHCl_3$ containing 1% of ethanol. One drop of acetic acid was added to each solution.



Scheme 2. Reactivity of compound **3**.

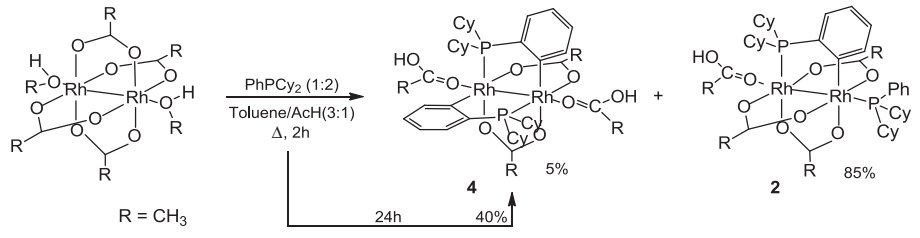
the reaction between dirhodium(II) tetraacetate and $PhPCy_2$ in a 1:1 ratio lead to a deep-blue solution, from which several compounds could be isolated after column chromatographic separation on silica (Scheme 1). An initial minor magenta-colored band eluted with hexane:CH_2Cl_2:acetic acid (40:20:1) was followed by a major blue fraction, whereas a green band stayed on the top of the column. The blue band was identified as the singly *ortho*-metalated complex $[Rh_2(\mu\text{-}O_2CCH_3)_3\{\mu\text{-}(C_6H_4)PCy_2\}(CH_3COOH)_2]$ (**1**) with two acetic acid ligands in axial position (Scheme 1). **1** was isolated in a moderate yield of 70%. The magenta-colored band consisted of a second singly *ortho*-metalated complex containing one acetic acid and one $PhPCy_2$ ligand in axial position, $[Rh_2(\mu\text{-}O_2CCH_3)_3\{\mu\text{-}(C_6H_4)PCy_2\}(CH_3COOH)(PhPCy_2)]$ (**2**). Though the coordination of the second phosphane is thinkable in any of the two axial positions of **1** resulting in the formation of two isomers, only the one with the phosphane axially coordinated to the rhodium atom bonded to the metalated carbon was observed. The formation of both isomers was observed for other phosphanes [9,23]. In the present case, the size of the cyclohexyl groups probably prevented the formation of the second isomer.

The isolation of this complex by column chromatography is remarkable, since the contact with eluate liquor containing acetic acid usually substitutes any axially coordinated phosphane ligand on rhodium(II) complexes [3]. **2** is an intermediate in the formation of a doubly *ortho*-metalated diphosphane rhodium(II) complex. Attempts to suppress the formation of **2** by altering the reaction time were unsuccessful. Consequently, unreacted dirhodium(II) tetraacetate was present on the column as a green band in all attempts to optimize the yield of **1**. On the other hand, **2** was formed quantitatively by an instantaneous reaction of **1** and one equivalent of $PhPCy_2$ in $CHCl_3$ (Scheme 1). It can be crystallized from hexane containing traces of CH_2Cl_2 as a magenta-colored powder.

In the $^{31}P\{^1H\}$ NMR spectrum, the phosphane ligand of **1** resonates in the typical range of mono-metalated rhodium(II) compounds at $\delta = 22.2$ ppm as a doublet of doublet [24]. ^1H and ^{13}C NMR spectra show only three signals for the acetate/acetic acid ligands in the ratio 1:2:2, indicating that the two molecules of acetic acid in axial position are equivalent on the NMR time scale. In the $^{31}P\{^1H\}$ NMR spectrum of **2**, the chemical shift of the *ortho*-metalated phosphane ligand changes only slightly upon coordination of the second molecule of $PhPCy_2$, whereas the axial phosphane ligand is strongly shielded by the rhodium atoms to a signal centered at $\delta = -16.2$ ppm. Both phosphane ligands resonate as ddd signals with a joint coupling constant $^3J(PP')$ of 12 Hz. In the electronic spectra of **1** and **2** (Fig. 1), distinct differences are observed in the visible region. A pale blue solution of **1** in $CHCl_3$ shows two merged bands of low intensity at 626 and 565 nm. Bands of singly *ortho*-metalated Rh_2-phosphane complexes in this region have previously been assigned to $\pi^*(Rh_2) \rightarrow \sigma^*(Rh_2)$ and $\pi^*(Rh_2) \rightarrow \delta^*(Rh{-}L_{eq})$ transitions, respectively [25–28]. In **1**, however, these bands are red-shifted by 42 and 128 nm in comparison with the bands of dirhodium(II) tetraacetate. Red-shifts of similar size have been observed previously [27]. Coordination of a second phosphane ligand to **1** in axial Rh–Rh direction creates the deeply magenta-colored complex **2**. In the UV/vis spectrum of **2**, this gives rise to an intensification of the band for the $\pi^*(Rh_2) \rightarrow \sigma^*(Rh_2)$ transition at $\lambda = 523$ nm. The second band is presumably hidden under an intense CT band which absorbs below 420 nm.

The irradiation of a $CHCl_3$ solution of **2** by an Hg–quartz lamp led to the rearrangement of the axial phosphane ligand into an equatorial position, while the free axial position was occupied by a molecule of acetic acid (Scheme 2). The complex formed in this reaction, $[Rh_2(\mu\text{-}O_2CCH_3)_2(\eta\text{-}O_2CCH_3)\{\mu\text{-}(C_6H_4)PCy_2\}(CH_3COOH)(PhPCy_2)]$ (**3**) was, however, only detected in solution by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. The rearrangement of the $PhPCy_2$ ligand into equatorial position caused a 50 ppm low-field shift of its signal in the $^{31}P\{^1H\}$ NMR spectrum. Other rhodium(II)/phosphane systems with this type of geometry have shown thermodynamic stability for many months. In contrast to this, **3** rearranged back to **2** over a period of 10 days to an extent of 60%. The other 40% of **2** reacted to a new species, identified as the doubly *ortho*-metalated compound $[Rh_2(\mu\text{-}O_2CCH_3)_2\{\mu\text{-}(C_6H_4)PCy_2\}_2(CH_3COOH)_2]$ (**4**) (Scheme 2). Since both bridging phosphane ligands now are chemically equivalent but magnetically not equivalent, the $^{31}P\{^1H\}$ NMR spectrum is an AA'XX' spin system with the signal centered at $\delta = 18.7$ ppm. The bridging acetate and the axially coordinated acetic acid ligands resonate as two singlets, respectively, in the ^1H and $^{13}C\{^1H\}$ NMR spectra.

Attempts to separate a mixture of **2** and **4** by column chromatography were not successful. To obtain **4** in pure form, a thermal synthesis was employed by reacting dirhodium(II) tetraacetate and



Scheme 3. Synthesis of **4**.

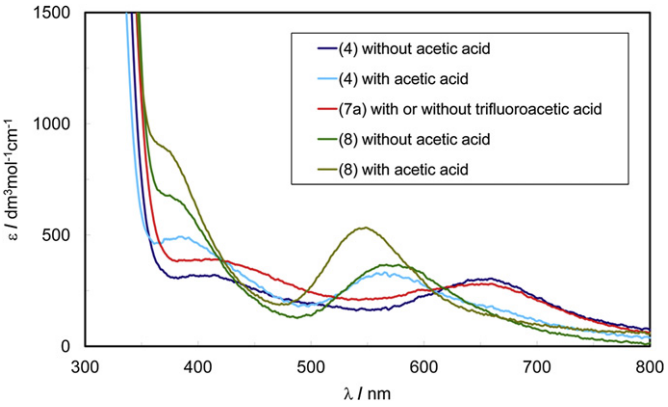
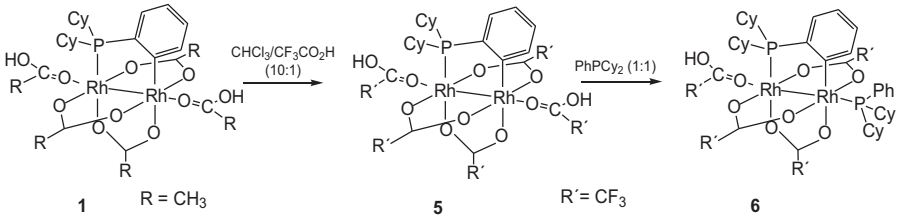


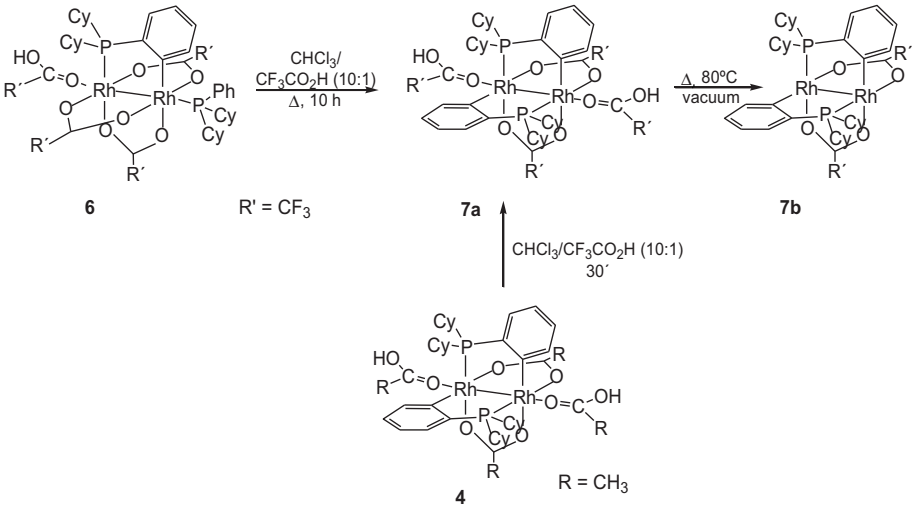
Fig. 2. UV/vis spectra of $[Rh_2(\mu\text{-}O_2CCH_3)_2\{\mu\text{-}(C_6H_4)PCy_2\}_2(CH_3COOH)_2]$ (**4**), $[Rh_2(\mu\text{-}O_2CCF_3)_2\{\mu\text{-}(C_6H_4)PCy_2\}_2(CF_3COOH)_2]$ (**7a**) and $[Rh_2(\mu\text{-}O_2CCH_3)_2\{\mu\text{-}(C_6H_4)PPh_2\}_2(CH_3COOH)_2]$ (**8**) dissolved in $CHCl_3$ containing 1% of ethanol. One drop of acetic/trifluoroacetic acid was added to the solution where indicated.



Scheme 4. Synthesis of **5** and **6**.

2 equivalents of $PhPCy_2$ for 2 h. However, the major product of this reaction in boiling toluene/acetic acid was complex **2**, which was isolated in 85% yield (Scheme 3). This again confirmed the unusual stability of **2** in thermal reactions. **4** was only present by approximately 5%. After prolonging the reaction time to 24 h, no signals of **2** were detected by $^{31}P\{^1H\}$ NMR spectroscopy. Due to the drastic conditions a considerable amount of the reaction system had begun to decompose in compounds which were not identified. Complex **4** was enriched in the reaction mixture only to 40%. However, it was now possible to isolate **4** by column chromatography on silica using CH_2Cl_2/hexane/acetic acid (100:100:1) as eluent. From this solvent mixture, **4** crystallizes in large, violet blocks.

During dissolution of **4** in $CHCl_3$ containing 1% of ethanol for UV/vis spectroscopic measurements, a color change from violet to green is observed. This color change is caused by an exchange of the axial acetic acid ligands for ethanol, however, upon addition of one drop of acetic acid, the violet color of **4** is restored. A similar color effect has been observed for the dissolution of $[Rh_2(\mu\text{-}O_2CCH_3)_2\{\mu\text{-}(C_6H_4)PPh_2\}_2(CH_3COOH)_2]$ (**8**) [2] in the $CHCl_3$/ethanol mixture, which changes from blue to violet by addition of acetic acid. In the visible part of the electronic spectra (Fig. 2), the color change of **4** from green to violet is displayed by a blue-shift of the $\pi^*(Rh_2) \rightarrow \sigma^*(Rh_2)$ transition from 652 nm to 564 nm. The corresponding blue-shift of **8** is much smaller (571 nm–546 nm). A



Scheme 5. Synthesis of **7a** and **7b**.

Table 1
Crystal data for $[Rh_2(\mu\text{-}O_2CCF_3)_3\{\mu\text{-}(C_6H_4)PCy_2\}(CF_3COOH)_2]$ (**5**).

Empirical formula	$C_{28}H_{28}F_{15}O_{10}PRh_2$
Formula weight	1046.29
Temperature (K)	153(2)
Crystal system	Triclinic
Space group	*P*–1 (number 2)
a (Å)	9.5439(8)
b (Å)	12.1501(10)
c (Å)	16.3073(13)
α (°)	90.1750(10)
β (°)	104.3930(10)
γ (°)	101.0410(10)
Cell volume (Å^3)	1795.2(3)
Z	2
D_{calc} (g cm^{-3})	1.936
μ(Mo Kα) (mm^{-1})	1.095
F(000)	1032
θ range (°)	2.86–23.28
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Reflections collected/unique	6974/4844 [$R_{int} = 0.0435$]
Reflections observed [$I > 2\sigma(I)$]	4844
Parameters	507
Goodness-of-fit on F^2	1.035
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0336$, $wR_2 = 0.0742$
R indices (all data)	$R_1 = 0.0456$, $wR_2 = 0.0799$
Largest diff. peak and hole	0.669 and −0.732 e Å^{-3}

similar propensity of the singly *ortho*-metalated complexes **1** and **2** to undergo color changes induced by exchange of the axial acetic acid ligand has not been observed.

An exchange of all acetate and acetic acid ligands in **1** for trifluoroacetate ligands was possible by stirring a solution of **1** in $CHCl_3/CF_3COOH$ (10:1) for 24 h at room temperature (Scheme 4). During the reaction the color changes from blue to green. The reaction product, $[Rh_2(\mu\text{-}O_2CCF_3)_3\{\mu\text{-}(C_6H_4)PCy_2\}(CF_3COOH)_2]$ (**5**), was purified from the liberated CH_3COOH by repeated evaporation from $CHCl_3/CF_3COOH$. The $^{19}F\{^1H\}$ NMR shows three singlets at −75.7, −75.3 and −74.9 ppm in a 2:1:2 ratio, confirming that two molecules of CF_3COOH are coordinated in axial position. In the ^1H NMR spectrum the carboxylic protons resonate as broad signals at 8.83 ppm. By slow evaporation of a $CDCl_3$ solution, dark-green single crystals of **5** suitable for an X-ray structure analysis were obtained (*vide infra*).

In full analogy to the transformation of **1** to **2**, the reaction of **5** with one equivalent of $PhPCy_2$ at room temperature afforded the singly *ortho*-metalated complex with a second phosphane ligand in axial position, $[Rh_2(\mu\text{-}O_2CCF_3)_3\{\mu\text{-}(C_6H_4)PCy_2\}(CF_3COOH)(PhPCy_2)]$ (**6**), which analogous to **2** was stable during elution from a silica column.

After heating a solution of **6** in $CHCl_3/CF_3COOH$ (10:1) to reflux for 10 h, the doubly *ortho*-metalated compound $[Rh_2(\mu\text{-}O_2CCF_3)_2\{\mu\text{-}(C_6H_4)PCy_2\}_2(CF_3COOH)_2]$ (**7a**) was detected by $^{31}P\{^1H\}$ NMR spectroscopy in 25% yield. Attempts to prolong the reaction time did not increase the yield of **7a**, but led to decomposition of the complexes (Scheme 5).

A much easier preparative access to **7a** was possible by the exchange of the acetate ligands of **4** by CF_3COO^- (Scheme 5). After 30 min of stirring **4** in $CHCl_3/CF_3COOH$ (10:1), the reaction was completed and **7a** was purified by column chromatography. Isolated in this way, **7a** contained two molecules of trifluoroacetic acid in axial position, which was shown by the presence of two signals in a 1:1 ratio in the $^{19}F\{^1H\}$ NMR and a broad signal at 5.5 ppm for the carboxylic protons in the ^1H NMR spectrum. In $CHCl_3$ solution containing 1% of ethanol, **7a** is stable against exchange of the axial trifluoroacetic acid ligands for ethanol, as judged by the unchanged position of the bands in the UV/vis spectrum (Fig. 2) before and after addition of trifluoroacetic acid. However, by heating **7a** at 80 °C for 1 h in vacuum, the axial coordinated CF_3COOH ligands were lost. A similar de-coordination of the axial ligands has been observed in the thermal treatment of dirhodium tetra(trifluoroacetate) [29]. In spite of its low solubility in chlorinated hydrocarbon solvents, the resulting complex $[Rh_2(\mu\text{-}O_2CCF_3)_2\{\mu\text{-}(C_6H_4)PCy_2\}_2]$ (**7b**) could be characterized by $^{19}F\{^1H\}$ NMR (one singlet at −75.0 ppm) and ^1H NMR spectroscopy, which did not show any signals of a ligand in axial position. Furthermore, the absence of axial ligands in **7b** was confirmed by a correct microanalysis.

3.2. Crystal structure of **5**

Details of the structure determination for complex **5** are shown in Table 1. Selected bond lengths and angles are shown in Table 2 and the molecular structure of **5** is displayed in Fig. 3. The structure of **5** can be viewed as a derivative of the paddlewheel structure of $[Rh_2(\mu\text{-}O_2CCF_3)_4]$ in which one of the trifluoroacetate ligands is replaced by a bridging dicyclohexylphenylphosphane ligand [29]. The phosphane ligand is coordinated via the phosphorus atom to one rhodium atom, while the phenyl ring is

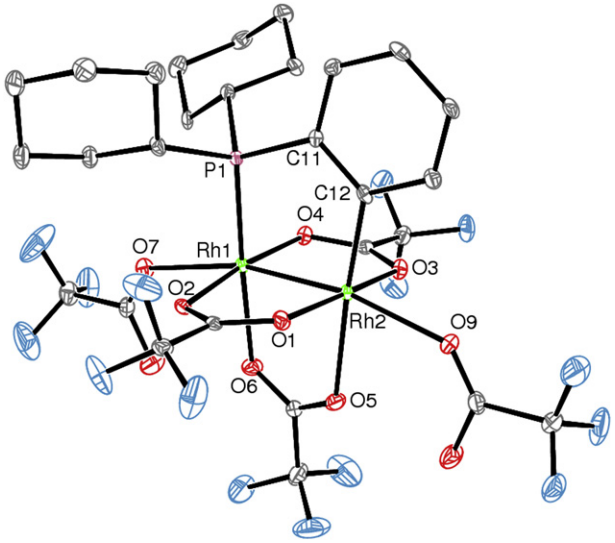


Fig. 3. Molecular structure of $[Rh_2(\mu\text{-}O_2CCF_3)_3\{\mu\text{-}(C_6H_4)PCy_2\}(CF_3COOH)_2]$ (**5**). The ellipsoids are drawn at the 30% probability level. H atoms have been removed for clarity.

Table 2
Selected bond lengths (Å) and angles (°) for $[Rh_2(\mu\text{-}O_2CCF_3)_3\{\mu\text{-}(C_6H_4)PCy_2\}(CF_3COOH)_2]$ (**5**).

Rh(1)–Rh(2)	2.4476(5)	Rh(2)–O(1)	2.055(3)
Rh(1)–P(1)	2.2311(12)	Rh(2)–O(3)	2.042(3)
Rh(1)–O(2)	2.045(3)	Rh(2)–O(5)	2.263(3)
Rh(1)–O(4)	2.044(3)	Rh(2)–O(9)	2.339(3)
Rh(1)–O(6)	2.212(3)	Rh(2)–C(12)	1.980(4)
Rh(1)–O(7)	2.400(3)		
Rh(2)–Rh(1)–P(1)	91.53(3)	Rh(2)–Rh(1)–O(7)	166.31(8)
Rh(1)–Rh(2)–C(12)	96.14(13)	Rh(1)–Rh(2)–O(9)	168.32(8)
P(1)–Rh(1)–O(7)	101.74(8)	C(12)–Rh(2)–O(9)	95.54(15)
P(1)–Rh(1)–O(6)	177.44(9)	C(12)–Rh(2)–O(5)	176.20(15)
O(2)–Rh(1)–O(4)	173.29(12)	O(1)–Rh(2)–O(3)	174.27(12)

coordinated in *ortho* position to the other rhodium atom. The framework of four bridging ligands is completed by two trifluoroacetic acid ligand coordinated in axial position to the rhodium atoms. Compared to the Rh–Rh distance of 2.3813(8) Å in the parent compound $[Rh_2(\mu\text{-}O_2CCF_3)_4]$ [29], the RhRh distance in **5** is slightly elongated (2.4476(5) Å). A similar Rh–Rh distance of 2.438(1) Å has been observed in a closely related complex to **5**, $[Rh_2(\mu\text{-}O_2CCF_3)_3\{\mu\text{-}(C_6H_4)PPh_2\}(CF_3COOH)_2]$, differing only in the nature of the organic substituents at the phosphorus atom [30]. However, the sterically more demanding cyclohexyl groups in **5** give rise to a stronger bending of the axial trifluoroacetic acid ligand away from the phosphane ligand. This is evidenced by a P(1)–Rh(1)–O(7) angle of 101.74(8)° compared to only 96.5(1)° in $[Rh_2(\mu\text{-}O_2CCF_3)_3\{\mu\text{-}(C_6H_4)PPh_2\}(CF_3COOH)_2]$. Another structural difference in both mono-metalated complexes is the conformation of the axial trifluoroacetic acid ligands. In $[Rh_2(\mu\text{-}O_2CCF_3)_3\{\mu\text{-}(C_6H_4)PPh_2\}(CF_3COOH)_2]$ it was found that only one trifluoroacetic acid ligand (coordinated to Rh(2)) formed an intramolecular interaction via hydrogen bonds to the trifluoroacetate ligand opposite to the bridging phosphane. The other trifluoroacetic acid ligand did not show any intramolecular interaction [30]. In contrast to this, both axial ligands in **5** show hydrogen bonding of their OH functions to the *trans*(P) trifluoroacetate ligand, resulting in O(5)–O(10) and O(6)–O(8) distances of 2.608 and 2.633 Å, respectively.

4. Conclusion

It has been demonstrated that the presence of cyclohexyl groups in the $PhPCy_2$ ligand has a significant impact on the chemistry of the system dirhodium tetraacetate/dicyclohexylphenylphosphane. The singly *ortho*-metalated complex $[Rh_2(\mu\text{-}O_2CCH_3)_3\{\mu\text{-}(C_6H_4)PCy_2\}(CH_3COOH)(PhPCy_2)]$ containing one axial phosphane ligand proved to be unusually thermodynamically stable, impeding the synthesis of the doubly *ortho*-metalated complex $[Rh_2(\mu\text{-}O_2CCH_3)_2\{\mu\text{-}(C_6H_4)PCy_2\}_2(CH_3COOH)_2]$ in high yield. Further work is required to determine if the cyclohexyl groups also exert an influence on the catalytic properties of the doubly *ortho*-metalated complexes.

Appendix A. Supplementary material

The crystallographic data for compound **5** have been deposited at The Cambridge Crystallographic Data Centre (reference number 916484). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References

[1] A.R. Chakravarty, F.A. Cotton, D.A. Tocher, J. Chem. Soc. Chem. Commun. (1984) 501–502.
[2] A.R. Chakravarty, F.A. Cotton, D.A. Tocher, J.H. Tocher, Organometallics 4 (1985) 8–13.
[3] F. Mohr, S.H. Privér, S.K. Bhargava, M.A. Bennett, Coord. Chem. Rev. 250 (2006) 1851–1888.
[4] P. Lahuerta, J. Payá, E. Peris, A. Aguirre, S. García-Granda, F. Gómez-Beltrán, Inorg. Chim. Acta 192 (1992) 43–49.
[5] P. Lahuerta, F. Estevan, in: Metal Clusters in Chemistry, vol. II, Wiley-VCH, Weinheim, 1999, p. 678 (and references therein).
[6] P. Lahuerta, J. Payá, M.A. Pellinghelli, A. Tiripicchio, Inorg. Chem. 31 (1992) 1224–1232.
[7] P. Lahuerta, E. Peris, M.A. Ubeda, S. García-Granda, F. Gómez-Beltrán, M.R. Díaz, J. Organomet. Chem. 455 (1993) C10–C12.
[8] A. Garcia-Bernabé, P. Lahuerta, M.A. Ubeda, S. García-Granda, P. Pertierra, Inorg. Chim. Acta 229 (1995) 203–209.
[9] F. Estevan, S. García-Granda, P. Lahuerta, J. Latorre, E. Peris, M. Sanaú, Inorg. Chim. Acta 229 (1995) 365–371.
[10] F. Estevan, A. Garcia-Bernabé, S. Gracía-Granda, P. Lahuerta, E. Moreno, J. Pérez-Prieto, M. Sanaú, M.A. Ubeda, J. Chem. Soc. Dalton Trans. (1999) 3493–3498.
[11] D.F. Taber, S.C. Malcolm, K. Bieger, P. Lahuerta, M. Sanaú, S.-E. Stiriba, J. Pérez-Prieto, M.A. Monge, J. Am. Chem. Soc. 121 (1999) 860–861.
[12] F. Estevan, K. Herbst, P. Lahuerta, M. Barberis, J. Pérez-Prieto, Organometallics 21 (2001) 950–957.
[13] M. Barberis, J. Pérez-Prieto, K. Herbst, P. Lahuerta, Organometallics 22 (2002) 1667–1673.
[14] F. Estevan, P. Lahuerta, J. Pérez-Prieto, M. Sanaú, S.-E. Stiriba, M.A. Ubeda, Organometallics 16 (1997) 880–886.
[15] F. Estevan, P. Lahuerta, J. Pérez-Prieto, I. Pereira, S.-E. Stiriba, Organometallics 17 (1998) 3442–3447.
[16] P. Lahuerta, E. Moreno, A. Monge, G. Muller, J. Pérez-Prieto, M. Sanaú, S.-E. Stiriba, Eur. J. Inorg. Chem. (2000) 2481–2485.
[17] M. Barberis, P. Lahuerta, J. Pérez-Prieto, M. Sanaú, Chem. Commun. (2001) 439–440.
[18] J. Pérez-Prieto, S.-E. Stiriba, E. Moreno, P. Lahuerta, Tetrahedron: Asymmetry 14 (2003) 787–790.
[19] F. Estevan, P. Lahuerta, J. Lloret, M. Sanaú, M.A. Ubeda, J. Vila, Chem. Commun. (2004) 2408–2409.
[20] P. Hirva, P. Lahuerta, J. Pérez-Prieto, Theor. Chem. Acc. 113 (2005) 63–68.
[21] J. Lloret, F. Estevan, P. Lahuerta, P. Hirva, J. Pérez-Prieto, M. Sanaú, Organometallics 25 (2006) 3156–3165.
[22] SHELXTL (Version 6.10), BRUKER, 2000.
[23] M.V. Borrachero, F. Estevan, P. Lahuerta, J. Payá, E. Peris, Polyhedron 12 (1993) 1715–1717.
[24] P. Lahuerta, J. Payá, X. Solans, M.A. Ubeda, Inorg. Chem. 31 (1992) 385–391.
[25] L. Natkaniec, F.P. Pruchnik, J. Chem. Soc. Dalton Trans. (1994) 3261–3266.
[26] F.P. Pruchnik, R. Starosta, P. Smoleński, E. Shestakova, P. Lahuerta, Organometallics 17 (1998) 3684–3689.
[27] F.P. Pruchnik, R. Starosta, T. Lis, P. Lahuerta, J. Organomet. Chem. 568 (1998) 177–183.
[28] R. Starosta, F.P. Pruchnik, Z. Ciunik, Polyhedron 25 (2006) 1994–2006.
[29] F.A. Cotton, E.V. Dikarev, X. Feng, Inorg. Chim. Acta 237 (1995) 19–26.
[30] S. García-Granda, P. Lahuerta, J. Latorre, M. Martinez, E. Peris, M. Sanaú, M.A. Ubeda, J. Chem. Soc. Dalton Trans. (1994) 539–544.