BIS(μ-CARBOXYLATO)DIENERHODIUM(I) COMPLEXES – SYNTHESIS, CHARACTERIZATION AND CATALYTIC ACTIVITY

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Dinuclear rhodium(I) η^2:η^2-cycloocta-1,5-diene (series **a**) and η^2:η^2-norborna-2,5-diene (series **b**) complexes with μ-$RCOO^-$ ligands, where R is linear $C_{21}H_{43}$ (complexes **1a**, **1b**), CH_2CMe_3 (**2a**, **2b**), 1-adamantyl (**3a**, **3b**) and benzyl (**4a**, **4b**), have been prepared and characterized by spectroscopic methods. Structures of complexes **2b**, **3a** and **4a** were determined by X-ray diffraction analysis. Complexes prepared show low to moderate catalytic activity in polymerization of phenylacetylene in THF giving high-*cis-transoid* polymers, but they show only oligomerization activity in dichloromethane.

Keywords: Rhodium; Rhodium complexes; Cycloocta-1,5-diene complexes; Norborna-2,5-diene complexes; Bis(μ-carboxylato) complexes; Polymerization; Polyacetylenes; X-ray structure.

Rhodium complexes attract permanent attention of many research groups because they catalyze high variety of chemical reactions such as hydroformylation, hydrosilylation, hydrogenation[1] of alkenes and polymerization of dienes, acetylenes and some other monomers[2]. Rh-based catalysts show a high tolerance to reaction solvents (alcohol, water, hydrocarbons, ionic liquids, etc.) and functional groups of reactants. Further advantage is the possibility of anchoring rhodium complexes on various supports such as mesoporous polybenzimidazole beads, polymer gels or mesoporous molecular sieves to give heterogeneous catalysts that are easy to separate from a reaction mixture[3].

In recent years, we have reported synthesis and catalytic activity of several new dinuclear rhodium complexes in hydroformylation of alkenes[4] ([{Rh(cod)}$_2$(μ-OC_6H_4-2-Me)$_2$] and [{Rh(nbd)}$_2$(μ-$OCOC_{21}H_{43}$)$_2$]) (cod is cycloocta-1,5-diene and nbd norborna-2,5-diene bound as η^2:η^2-ligands),

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atom transfer radical polymerization of styrene and methyl methacrylate[5] ([{Rh(cod)}$_2$(μ-OC$_6$H$_4$-4-Me)$_2$] and [{Rh(cod)}$_2$(μ-OCOC$_{21}$H$_{43}$)$_2$]), and polymerization of substituted acetylenes[6]. We also reported the isomerism of dinuclear μ-(2-methylphenolato) complex [{Rh(cod)}$_2$(μ-OC$_6$H$_4$-2-Me)$_2$] occurring due to steric effects of ortho-methyl groups and characterized dynamic processes taking place in this complex: rotation of the phenyl ring along O–C$_{ring}$ axis and a virtual rotation of cod ligand[7]. In this contribution we report preparation and structure of some new dinuclear μ-carboxylato bridged rhodium diene complexes (Fig. 1) and their activity in polymerization and oligomerization of phenylacetylene.

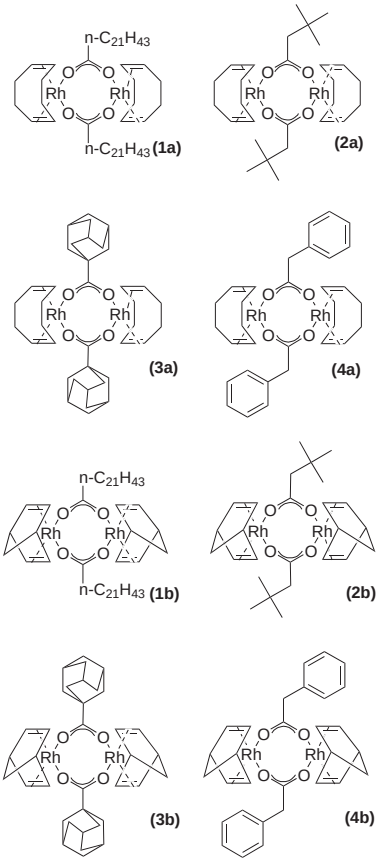


FIG. 1
Prepared rhodium(I) complexes

EXPERIMENTAL

General

$RhCl_3 \cdot xH_2O$ (Safina Vestec), cycloocta-1,5-diene, norborna-2,5-diene, adamantane-1-carboxylic acid, phenylacetylene (PhA), docosanoic (behenic) acid, 3,3-dimethylbutanoic acid and phenylacetic acid (Aldrich), $AgNO_3$ p.a., NaOH, methanol, ethanol (Lachema) were used as supplied. Dichloromethane, hexane and pentane (all Lachema, Czech Republic) were distilled from P_2O_5 and stored under argon atmosphere above 4Å molecular sieves. Tetrahydrofuran (THF) (Riedel-deHaen, 99.5%) was distilled from CuCl and CaH_2 and stored under argon. Acetone (Lachema) was distilled from $KMnO_4$ to remove reducing matters. Starting compounds di(μ-chloro)bis[(η^2:η^2-cycloocta-1,5-diene)rhodium(I)] and di(μ-chloro)bis[(η^2:η^2-norborna-2,5-diene)rhodium(I)] were prepared from $RhCl_3 \cdot xH_2O$ using the procedure already described in literature[8].

^1H and $^{13}C\{^1H\}$ NMR spectra were measured on a Varian ^{UNITY}*INOVA* 400 in $CDCl_3$ solutions unless stated otherwise. Chemical shifts δ are reported in ppm relative to tetramethylsilane (^1H) or the solvent peak (for ^{13}C, 77.00 ppm). Coupling constants, *J*, are given in Hz and they were obtained by the first-order analysis. COSY experiments were recorded in the absolute value mode using the standard two-pulse sequence. HSQC and HMBC were performed as gradient experiments. All 2D experiments were recorded with spectral windows 5 000 Hz for protons and 25 000 Hz for carbons. Infrared spectra were recorded on a Nicolet Magna 760 IR instrument equipped with Inspector IR using both undiluted and KBr-diluted samples. The diffuse reflectance technique (DRIFT) (128 or more scans at resolution 4 cm^{-1}) was used.

Size exclusion chromatography (SEC) measurements were carried out using a HP 1100 liquid chromatograph fitted with a diode array detector (DAD; λ = 254 nm). A series of two PL-gel columns (Mixed B and Mixed C, Polymer Laboratories, U.K.) and THF (flow rate 0.7 ml/min) were used. Number- and weight-average molecular weights, M_n and M_w, respectively, relative to PS standards were calculated using the calibration curve method. GC/MS analyses were done on a Shimadzu QP 2010 Instrument.

X-ray Structure Determination

A measured crystal was mounted on a glass fiber with epoxy cement and its structure was determined using a Nonius KappaCCD four-circle diffractometer with a CCD area detector, monochromatized MoKα radiation (λ = 0.71073 Å) at 150(2) K and the HKL program package for the data analysis. Crystallographic details are summarized in Table I. Empirical absorption corrections were applied (multiscan from symmetry-related measurements) for **2b**. The structures were solved by the direct method (SIR92) and refined by a full-matrix least-squares procedure based on F^2 (SHELXL97). Hydrogen atoms were generally fixed into idealized positions (riding model) and temperature factors $H_{iso}(H) = 1.2\,U_{eq}$(pivot atom) were assigned; for the methyl groups, a multiple of 1.5 was chosen. For **4a** and **2b** crystals, the hydrogen atoms of the –CH=CH– group were found on difference Fourier maps and refined isotropically. The final difference maps displayed no peaks of chemical significance. A disorder observed for **3a** was found to be owing to rotation of adamantyl moieties acquiring two positions with occupation factors 0.75 and 0.25, respectively. Their bond distances and angles were restrained to be equal; all atoms were refined isotropically.

TABLE I
Crystal data and structure refinement for complexes **2b**, **3a** and **4a**

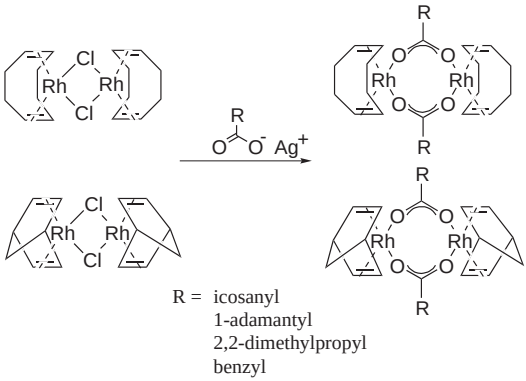
Parameter	**2b**	**3a**	**4a**
Formula	$C_{26}H_{38}O_4Rh_2$	$C_{38}H_{54}O_4Rh_2 \cdot CDCl_3$	$C_{32}H_{38}O_4Rh_2$
Color	red	orange	red
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)
a, Å	16.1910(1)	13.0870(2)	13.1350(3)
b, Å	13.1800(2)	17.3330(2)	21.7570(8)
c, Å	12.9060(2)	16.8100(2)	9.7500(5)
β, °	110.3170(6)	104.7670(7)	95.913(2)
Z	4	4	4
μ, mm^{-1}	1.306	1.153	1.227
D_x, Mg m^{-3}	1.595	1.621	1.659
Crystal size, mm^3	0.18 × 0.15 × 0.12	0.35 × 0.15 × 0.1	0.2 × 0.05 × 0.007
Crystal shape	rod	plate	plate
θ range, deg	1–27.5	1–27.5	1–27.5
T_{min}, T_{max} [a]	0.793, 0.851		
No. of measured reflections	49811	65690	22832
No. of unique reflections; R_{int}	5907; 0.050	8441; 0.098	4848; 0.076
No. of observed reflections [$I > 2\sigma(I)$]	5117	7295	3681
No. of parameters	328	432	375
S [b] (all data)	1.067	1.020	1.030
Final R [b] [$I > 2\sigma(I)$]	0.028	0.038	0.039
$wR2$ [b] (all data)	0.061	0.091	0.063
w_1/w_2 [c]	0.0231; 1.8676	0.0328; 10.3580	0.0056; 1.7842
Δρ, max., min., e $Å^{-3}$	0.608; –0.809	1.267; –0.807	0.400; –1.281

[a] Correction by SORTAV program. [b] Definitions: $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(w(F_o^2)^2)]^{1/2}$, $S = [\Sigma(w(F_o^2 - F_c^2)^2)/(N_{reflns} - N_{params})]^{1/2}$. [c] Weighting scheme $w = [\sigma^2(F_o^2) + w_1P + w_2P]^{-1}$. $P = [\max(F_o^2,0) + 2F_c^2]/3$. $R_{int} = \Sigma|F_o^2 - F_o^2(\text{mean})|/\Sigma F_o^2$ (summation is carried out only if more than one symmetry equivalents were averaged).

CCDC 687097, 687098 and 687099 (for **2b**, **3a** and **4a**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Synthesis of Rhodium Complexes. General Procedure

All complexes were prepared by the ultrasound-assisted reaction of $[\{Rh(cod)\}_2(\mu\text{-}Cl)_2]$ or $[\{Rh(nbd)\}_2(\mu\text{-}Cl)_2]$ with ten-fold excess of the silver salt of corresponding carboxylic acid (Scheme 1).



SCHEME 1
Synthesis of $[\{Rh^{I}(diene)\}_2(\mu\text{-carboxylato})_2]$ complexes

Preparation of Silver Carboxylates

Silver alkanecarboxylates (except for silver docosanoate) were prepared by the reaction of sodium salt of corresponding acid (24 mmol) with aqueous solution silver nitrate (5.1 g, 30 mmol in 100 ml of water) in the dark at room temperature. Precipitated silver salt was repeatedly washed with water to remove unreacted silver nitrate, then extracted with ethanol in a Soxhlet extractor to remove traces of unreacted carboxylic acid and, finally, dried in vacuum for 12 h. Silver docosanoate was prepared in the dark at 50 °C by gradual addition of a warm solution of docosanoic acid (8.2 g, 24 mmol) in ethanol (500 ml) to a warm solution of silver nitrate (5.1 g, 30 mmol) in 15% aqueous ammonium hydroxide (500 ml). Precipitated silver docosanoate was worked up as described above.

Preparation of Rhodium Complexes

Procedure 1 (in water): Corresponding silver salt (2.2 mmol) was suspended in water (10 ml), rhodium(I) μ-chloro complex, $[\{Rh(nbd)\}_2(\mu\text{-}Cl)_2]$ (100 mg, 0.22 mmol) or $[\{Rh(cod)\}_2(\mu\text{-}Cl)_2]$ (108 mg, 0.22 mmol), was added and the resulting suspension was sonicated (Elmasonic E30H ultrasonic bath, maximum power) under argon in the capped glass vial for 15 min. Then water was removed from the reaction mixture on a vacuum rotary evaporator, the

crude product was dissolved in THF (100 ml) and the byproduct, AgCl, was filtered off. The resulting THF solution was evaporated on a vacuum rotary evaporator. This procedure was first reported[4,5] for preparation of complexes **1b** and **3b**, respectively.

Procedure 2 (in CH_2Cl_2): A corresponding silver salt (2.2 mmol) was suspended in CH_2Cl_2 (5 ml) and a solution of a rhodium(I) μ-chloro complex (0.22 mmol) in CH_2Cl_2 (5 ml) was added. Instantaneous color change of the reaction mixture proved fast course of the reaction. The mixture was allowed to react for 15 min in ultrasound bath and then treated as given above.

Crystallization: Crystallizations were performed typically in screw thread glass vial or in NMR cuvette. The crude complex was dissolved in the minimum amount of the "better" solvent (CH_2Cl_2, THF). Solution of the complex was cooled down to –15 °C. Then volume excess of the "worse" previously cooled solvent (hexane, diethyl ether, acetone) was carefully added by syringe to cover the complex solution level. The vial was placed to the freezer at –24 °C for 24–72 h. Three solvent systems were examined for crystallization of complexes prepared: (i) CH_2Cl_2/alkane (pentane or hexane); this system is highly efficient in purification of all complexes prepared and, therefore, it is the first method of choice. However, it did not provide crystals suitable for X-ray analysis. (ii) CH_2Cl_2/diethyl ether and THF/acetone, only the latter gave in some cases (**2b**, **4a**) crystals suitable for X-ray diffraction measurements. Crystals of the complex **3a**, suitable for X-ray diffraction analysis, were obtained by slow evaporation of $CDCl_3$ in NMR cuvette. A slow evaporation of solvent from the complex solution in dichloromethane[6] did not give any crystal suitable for X-ray diffraction measurements. (Numbering of carbon atoms in the carboxylate ligand, see Fig. 2).

$[\{Rh(cod)\}_2(\mu\text{-Docosanoato})_2]$ (**1a**)

Crystallization by diffusion of cold pentane into cold dichloromethane solution gave orange microcrystalline powder in isolated yield 175 mg (78%; procedure 1). For $C_{60}H_{110}O_4Rh_2$ (1101.36) calculated: 65.43% C, 10.07% H; found: 66.29% C, 10.01% H. ^{1}H NMR ($CDCl_3$): 0.88 t, 6 H, J = 6.8 (CH_3, anion); 1.05–1.40 m, 76 H ($C^{3\text{-}20}H_2$, anion); 1.56 bs, 4 H (C^2H_2, anion); 1.70–1.90 m, 8 H (CH_2, cod); 2.63 bs, 4 H (CH_2, cod); 2.83 bs, 4 H (CH_2, cod); 4.11 bs, 8 H (CH=, cod). ^{13}C NMR ($CDCl_3$): 14.1 (CH_3); 22.7 (CH_2, anion); 26.3 (C^3H_2, anion); 29.1–29.7, 31.9 (CH_2, anion); 37.5 (C^2H_2, anion); 31.1 (CH_2, cod); 73.6, 80.6 (CH=, cod); 185.3 (COO). FT IR (KBr diluted sample): 672 m, 742 m, 772 w, 816 m, 863 w, 875 m,

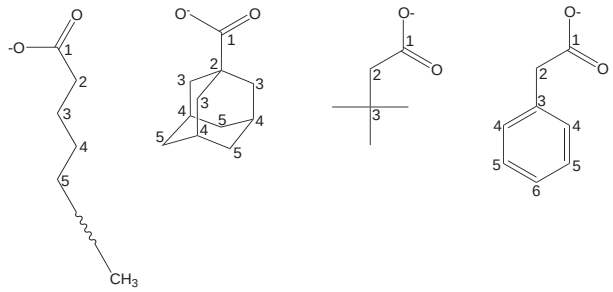


FIG. 2
Numbering of carbon atoms in the carboxylate ligands

889 m, 956 m, 996 m, 1107 m, 1227 w, 1297 m, 1325 m, 1420 s, 1474 s, 1577 vs, 1855 vs, 2928 vs.

[{Rh(nbd)}$_2$(μ-Docosanoato)$_2$] (**1b**)

Crystallization by diffusion of cold pentane into cold dichloromethane solution gave red-orange microcrystalline powder in isolated yield 144 mg (62%; procedure 1). For $C_{58}H_{102}O_4Rh_2$ (1068.60) calculated: 65.13% C, 9.62% H; found: 64.98% C, 9.73% H. ^{1}H NMR ($CDCl_3$): 0.81 t, 6 H, J = 7.0 (CH_3, anion); 1.23 bs, 4 H (CH_2, nbd); 1.26 m, 72 H ($C^{4\text{-}20}H_2$, anion); 1.29 bs, 4 H (C^3H_2, anion); 1.89 bs, 4 H (C^2H_2, anion); 4.01 s, 8 H (CH=, nbd); 4.07 bs, 4 H (CH, nbd). ^{13}C NMR ($CDCl_3$): 14.1 (CH_3, anion); 22.7 (CH_2, anion); 26.2 (C^3H_2, anion); 29.1 (C^4H_2, anion); 29.7 (CH_2, anion); 30.9 (CH_2, anion); 37.1 (C^2H_2, anion); 50.2 (CH_2, nbd); 50.6 (CH=, nbd); 60.1 (CH, nbd); 184.5 (COO). FT IR (KBr diluted sample): 719 w, 881 vw, 995 vw, 1032 vw, 1112 vw, 1168 vw, 1303 w, 1396 w, 1420 w, 1471 w, 1562 s, 2849 s, 2916 vs.

[{Rh(cod)}$_2${μ-(3,3-Dimethyl)butanoato}$_2$] (**2a**)

Crystallization by diffusion of cold pentane into cold dichloromethane solution gave yellow microcrystalline powder in isolated yield 98 mg (74%; procedure 1). For $C_{28}H_{46}O_4Rh_2$ (652.36) calculated 51.54% C, 7.11% H; found 52.40% C, 7.29% H. ^{1}H NMR ($CDCl_3$): 0.83 m, 18 H (CH_3, anion); 1.75 m, 4 H (CH_2, cod); 1.85 bs, 4 H (C^2H_2, anion); 1.90 bs, 4 H (CH_2, cod); 2.60 bs, 4 H (CH_2, cod); 2.86 bs, 4 H (CH_2, cod); 4.13 bs, 4 H (CH=, cod); 4.19 bs, 4 H (CH=, cod). ^{13}C NMR ($CDCl_3$): 29.7 (CH_3, anion); 30.5 (C^3, anion) overlap with (CH_2, cod); 30.5 (CH_2, cod) overlap with (C^3, anion); 31.3 (CH_2, cod); 51.0 (C^2H_2, anion); 73.4, 80.4 (CH=, cod); 183.6 (COO). FT IR (KBr diluted sample): 411 m, 451 w, 476 m, 491 m, 513 w, 541 w, 636 s, 734 s, 777 m, 793 s, 817 m, 833 m, 874 s, 892 m, 953 s, 996 s, 1033 w, 1044 w, 1078 m, 1150 m, 1175 m, 1201 s, 1214 s, 1235 s, 1277 s, 1305 s, 1326 s, 1365 s, 1407 vs, 1438 vs, 1474 vs, 1572 vs, 2640 w, 2709 w, 2836 s, 2887 vs, 2955 vs, 3004 m.

[{Rh(nbd)}$_2${μ-(3,3-Dimethyl)butanoato}$_2$] (**2b**)

Crystallization by diffusion of cold pentane into cold dichloromethane solution gave red crystalline needles in isolated yield 85 mg (63%; procedure 1). For $C_{26}H_{38}O_4Rh_2$ (620.40) calculated 50.34% C, 6.17% H; found 51.22% C, 6.01% H. ^{1}H NMR ($CDCl_3$): 0.78 s, 18 H (CH_3, anion); 1.31 m, 4 H (CH_2, nbd); 1.82 bs, 4 H (C^2H_2, anion); 4.09 bs, 8 H (CH=, nbd); 4.15 bs, 4 H (CH, nbd). ^{13}C NMR ($CDCl_3$): 29.6 (CH_3, anion); 30.4 (C^3, anion); 48.4 (CH_2, nbd); 50.5 (C^2H_2, anion); 50.6, 53.6 (CH=, nbd); 57.1, 63.2 (CH, nbd); 182.7 (COO). FT IR (KBr diluted sample): 414 w, 505 w, 565 w, 650 w, 734 w, 773 w, 799 w, 806 w, 883 w, 926 w, 1153 w, 1169 w, 1202 w, 1236 w, 1277 w, 1303 w, 1364 w, 1405 s, 1432 m, 1474 w, 1563 vs, 2864 w, 2909 m, 2948 m, 3042 w, 3056 w.

[{Rh(cod)}$_2${μ-(Adamantane-1-carboxylato)}$_2$] (**3a**)

Crystallization by diffusion of cold pentane into cold dichloromethane solution gave yellow microcrystalline powder in isolated yield 114 mg (72%; procedure 1). For $C_{38}H_{54}O_4Rh_2$ (780.22) calculated: 58.47% C, 6.97% H; found: 59.02% C, 6.62% H. ^{1}H NMR ($CDCl_3$): 1.55–2.03 m, 30 H (adamantane) overlap with (CH_2, cod); 1.55–2.03 m, 8 H (CH_2, cod) over-

lap with (H, adamantane); 2.62 m, 4 H (CH_2, cod); 2.81 m, 4 H (CH_2, cod); 4.13 bs, 4 H (CH=, cod); 4.19 bs, 4 H (CH=, cod). ^{13}C NMR ($CDCl_3$): 28.4 (C^4H, adamantane); 30.5, 31.3 (CH_2, cod); 36.7 (C^5H_2, adamantane); 39.6 (C^3H_2, adamantane); 41.8 (C^2, adamantane); 66.4, 72.0, 80.8, 87.5 (CH=, cod); 189.1 (COO). FT IR (KBr diluted sample): 419 s, 425 s, 498 s, 579 m, 679 s, 748 w, 763 m, 779 w, 790 w, 818 m, 866 m, 877 s, 892 m, 906 m, 956 m, 978 m, 995 m, 1066 s, 1089 m, 1102 m, 1113 m, 1175 m, 1183 m, 1212 w, 1258 w, 1290 sh, 1310 s, 1326 m, 1343 w, 1365 w, 1412 vs, 1451 m, 1470 w, 1497 w, 1531 w, 1563 vs, 2655 w, 2677 w, 2847 vs, 2902 vs.

[{Rh(nbd)}$_2${μ-(Adamantane-1-carboxylato)}$_2$] (**3b**)

Crystallization by diffusion of cold pentane into cold dichloromethane solution gave orange-red microcrystalline powder in isolated yield 106 mg (65%; procedure 1). For $C_{36}H_{46}O_4Rh_2$ (748.58) calculated: 57.76% C, 6.19% H; found 58.02% C, 6.38% H. ^1H NMR ($CDCl_3$): 1.30 s, 4 H (CH_2, nbd); 1.54 s, 12 H (C^5H_2, adamantane); 1.57 s, 12 H (C^3H_2, adamantane); 1.84 m, 6 H (C^4H, adamantane); 4.02 s, 8 H (CH=, nbd); 4.20 bs, 4 H (CH, nbd). ^{13}C NMR ($CDCl_3$): 28.3 (C^4H, adamantane); 36.7 (C^5H_2, adamantane); 39.5 (C^3H_2, adamantane); 41.4 (C^2, adamantane); 48.3 (CH=, nbd); 50.6 (CH_2, nbd); 53.5 (CH=, nbd); 59.9 (CH, nbd); 188.3 (COO). FT IR (KBr diluted sample): 494 m, 679 m, 764 m, 791 m, 798 m, 928 m, 977 w, 1033 w, 1044 w, 1069 w, 1091 m, 1101 w, 1113 w, 1155 w, 1172 w, 1181 w, 1236 w, 1252 w, 1260 w, 1301 m, 1310 s, 1343 w, 1365 m, 1396 s, 1413 vs, 1431 m, 1451 m, 1472 w, 1499 w, 1507 w, 1551 vs, 1560 s, 2849 s, 2930 vs, 2995 m, 3041 w, 3058 w, 3470 w.

[{Rh(cod)}$_2$(μ-Phenylacetato)$_2$] (**4a**)

Crystallization by diffusion of cold pentane into cold dichloromethane solution gave orange crystalline needles in isolated yield 96 mg (68%; procedure 1). For $C_{32}H_{38}O_4Rh_2$ (692.09) calculated: 55.51% C, 5.53% H; found: 55.02% C, 5.62% H. ^1H NMR ($CDCl_3$): 1.74 m, 8 H (CH_2, cod); 2.65–2.81 m, 8 H (CH_2, cod); 3.29 s, 4 H (CH_2, anion); 3.98 bs, 8 H (CH=, cod); 7.07–7.26 m, 10 H (phenyl). ^{13}C NMR ($CDCl_3$): 30.8 (CH_2, cod); 44.4 (C^2H_2, anion); 73.8, 80.7 (CH=, cod); 126.1 (C^6, arom); 128.0 (C^4, arom); 128.9 (C^5, arom); 136.8 (C^3, arom); 182.5 (COO). FT IR (KBr diluted sample): 492 m, 518 w, 563 w, 568 m, 696 s, 712 s, 728 s, 776 w, 816 m, 846 w, 866 m, 875 w, 890 w, 956 w, 996 m, 1029 m, 1075 m, 1152 m, 1173 w, 1192 s, 1211 m, 1297 s, 1326 m, 1403 vs, 1453 m, 1470 m, 1495 m, 1545 w, 1578 vs, 2833 s, 2879 s, 2942 s, 3000 m, 3028 w, 3063 m, 3078 w.

[{Rh(nbd)}$_2$(μ-Phenylacetato)$_2$] (**4b**)

Crystallization by diffusion of cold pentane into cold dichloromethane solution gave red-orange microcrystalline powder in isolated yield 97 mg (68%; procedure 1). For $C_{30}H_{30}O_4Rh_2$ (660.03) calculated: 54.56% C, 4.58% H; found: 54.72% C, 4.33% H. ^1H NMR ($CDCl_3$): 1.28 m, 4 H (CH_2, nbd); 3.20 s, 4 H (C^2H_2, anion); 3.99 m, 8 H (CH=, nbd); 4.09 bs, 4 H (CH, nbd); 7.0 d, 4 H (C^4H, arom); 7.13 m, 2 H (C^6H-arom); 7.17 s, 4 H (C^5H, arom). ^{13}C NMR ($CDCl_3$): 43.8 (C^2H_2, anion); 49.5 bs (CH_2, nbd); 50.5 (CH=, nbd); 60.1 (CH, nbd); 126.0 (C^6, arom); 128.0 (C^4, arom); 128.8 (C^5, arom); 136.6 (C^3, arom); 181.7 (COO). FT IR (KBr diluted sample): 489 w, 641 w, 694 w, 711 m, 723 m, 759 w, 776 w, 816 w, 1075 w, 1155 w, 1173 w, 1194 w, 1209 w, 1226 w, 1297 w, 1305 w, 1324 w, 1388 w,

1401 s, 1420 m, 1453 w, 1468 w, 1544 m, 1578 vs, 2832 m, 2984 w, 2998 w, 3027 w, 3063 w.

Catalytic Hydrogenation

Catalytic hydrogenation of styrene and dec-1-ene was performed at atmospheric pressure of hydrogen. In the 100-ml Schlenk flask connected to the argon/vacuum manifold and equipped with magnetic stirring bar, 30 ml of dry freshly distilled diethyl ether and 0.52 g of styrene or 0.7 g of dec-1-ene (5 mmol) were added. The solution was degassed using three standard liquid nitrogen-assisted vacuum/argon cycles. Previously degassed solution of 267 mg of complex **1a** or 187 mg of complex **3b** (0.25 mmol) in 20 ml freshly distilled dry diethyl ether was added by stainless steel capillary to the Schlenk flask. The system was again cooled down by liquid nitrogen, evacuated and flushed with hydrogen. The hydrogen consumption was monitored by the pressure decrease method and the liquid part of the reaction mixture was analysed using GC/MS technique (sampling times: 10, 60, 120, 180 and 240 min).

Polymerization and Oligomerization of Phenylacetylene

Polymerization experiments were carried out in glass screwthread vials equipped with magnetic stirrer at room temperature. The reaction was started by mixing solutions (2 ml each) of the monomer and the respective catalyst in THF or CH_2Cl_2 (initial monomer concentration $[M]_0$ = 0.6 mol l^{-1}, initial monomer to Rh mole ratio $[M]_0/[Rh]$ = 200). Polymerization was quenched by pouring the reaction mixture into the ten-fold volume excess of methanol, the precipitated polymer was isolated by the sedimentation in centrifuge (5000 rpm). The precipitate was washed several times with methanol (centrifugation) and dried to the constant weight in vacuum (15 torr) at room temperature. Evaporation of solvents and the unreacted monomer from the supernatants (all liquid fractions received during the polymer isolation) provided oligomeric byproducts; the yields were determined gravimetrically. Isolated oligomeric fraction was analysed by SEC to determine relative ratios of linear oligomers and cyclotrimers. In SEC chromatograms, always two peaks were obtained: (i) The sharp peak, the retention time of which corresponded to that of cyclotrimers (verified by SEC analysis of the standard 1,3,5-triphenylbenzene (Aldrich) and by GC/MS analyses of oligomers) and (ii) the broader peak (molecular weight corresponding to the maximum of the peak, M_p = (1.0–2.0) × 10^3) that was ascribed to the linear PhA oligomers.

RESULTS AND DISCUSSION

Preparation of Complexes

Different reaction media were tested for the preparation of complex **3b**. The μ-carboxylatorhodium(I) complexes prepared by procedure 1 (in water) are of higher purity than those prepared in CH_2Cl_2 as evidenced in Fig. 3 in which ^{1}H NMR spectra of crude samples of **3b** prepared by different procedures are compared. NMR signals characteristic of dinuclear rhodium(I) species (for spectrum of **3b** prepared in water see Fig. 3b) are accompanied by a

series of signals of impurities in the spectrum of the sample prepared in CH_2Cl_2 (for spectrum see Fig. 3a). The observed signals of impurities can be ascribed to the presence of oligomeric or polynuclear Rh(I) species, the existence of which is described in literature[9]. When the reaction is done in water, it must proceed in highly dilute solutions because both reactants, rhodium(I) μ-chloro complex and silver carboxylate, are nearly insoluble in water. Thus, the probability of formation of oligomeric Rh(I) species comprising three or more Rh atoms linked by intermolecular μ-carboxylato bridges is strongly reduced. On the other hand, rather high concentration of Rh(diene) species in the system with CH_2Cl_2 (procedure 2), a good solvent for the species, facilitates undesirable formation of oligomeric (polynuclear) Rh(I) species. Therefore, the ultrasound-assisted procedure 1, which exploits water as the reaction medium, is favorable. Also, it is worth mentioning that Rh(nbd) species show a considerably higher tendency to form oligomers compared with the Rh(cod) species. Attempts to prepare crystallizable Rh(nbd) complexes in CH_2Cl_2 solvent mostly failed owing to a formation of a high amount of the oligomeric Rh(nbd) species.

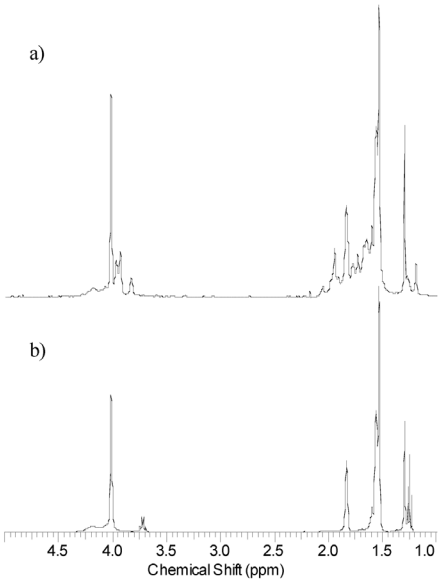


FIG. 3
A comparison of ^{1}H NMR spectra of a samples of the crude complex **3b** (before crystallization) prepared by sonication in dichloromethane (a) and water (b) (the assignment is given in Experimental)

Structure of Complexes

The molecular structures (ORTEP drawing) of **2b**, **3a** and **4a** are shown in Figs 4, 5 and 6 and crystallographic data are given in Table I.

The geometric parameters are not exceptional: the structure of **2b** is similar to that of the $[\{Rh(nbd)\}_2(\mu\text{-}CH_3CO_2)_2]$ complex[10] and those of **3a** and **4a** are close to the analogous $[\{Rh(cod)\}_2(\mu\text{-salicylato})_2]$ complex[11]. The coordination environments of the Rh atoms formed by two oxygens and two –C=C– double bonds are nearly square planar in **3a** and **4a**. Significant deviation from 90° observed for **2b** (cg1-Rh-cg2 72.62(11)°; cg = centroid of the –C=C– double bond) follows from rigidity of norborna-2,5-diene. The angles between coordination planes (defined by Rh, two oxygens and two corresponding centroids (cg) are 58.70(12)°, 59.71(15)° and 48.61(8)° for **3a**, **4a** and **2b**, respectively. These butterfly structures result in Rh(1)–Rh(2) distances 3.3026(3), 3.3868(4) and 3.0636(2) Å for **3a**, **4a** and **2b**, respectively, suggesting the absence of a direct metal–metal bonding; similar distances were found for the bis(acetato)[10] (3.105 Å) and bis(salicylato)[11] (3.325 Å) analogs. This conclusion is supported by the histogram of Rh···Rh distances constructed from data found for all complexes containing two Rh atoms

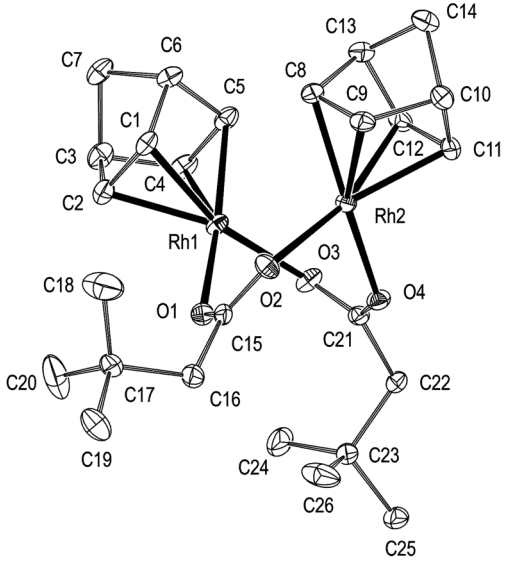


FIG. 4
ORTEP drawing for complex **2b**. The displacement ellipsoids are drawn on 30% probability level. Hydrogen atoms are omitted for clarity

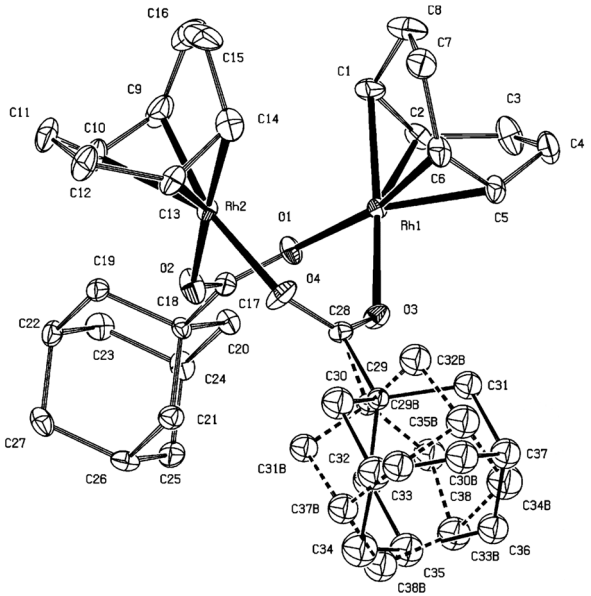


FIG. 5
ORTEP drawing for complex **3a**. The displacement ellipsoids are drawn on 30% probability level. Hydrogen atoms are omitted for clarity

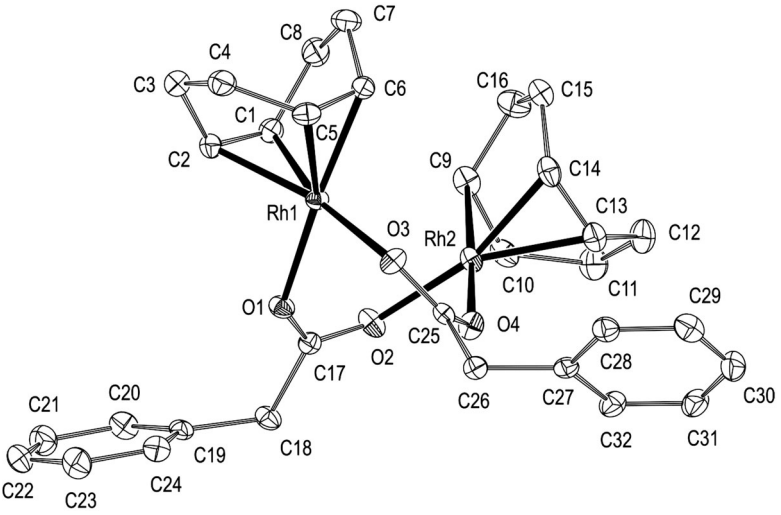


FIG. 6
ORTEP drawing for complex **4a**. The displacement ellipsoids are drawn on 30% probability level. Hydrogen atoms are omitted for clarity

bridged by at least one carboxylate (Fig. 7) in the Cambridge Crystallographic Data Centre. A sharp maximum at 2.42 Å belonging to complexes with the Rh–Rh bond is not shown in Fig. 7. After a gap of 0.3 Å, there are 23 hits with this parameter distributed in relatively large range from 2.9 to 3.5 Å, as the non-bonding distance is strongly affected by steric requirements of complementary ligands. As it can be seen, the Rh(1)···Rh(2) distance in the Rh(nbd) complex **2b** is about ~0.3 Å lower than the distances found for the Rh(cod) complexes **3a** and **4a**.

Catalytic Activity of [{Rh(diene)}$_2$(μ-OCOR)$_2$] Complexes

In our previous paper[4], we reported the activity of **1b** and **3b** in hydroformylation of olefins. In this contribution, the catalytic activity of these two complexes was also tested in hydrogenation of dec-1-ene and styrene using diethyl ether as solvent and standard pressure of hydrogen (see Experimental). No significant traces of hydrogenated products were observed.

Polymerization of Phenylacetylene with [{Rh(diene)}$_2$(μ-OCOR)$_2$] Complexes

All complexes prepared were tested as to their activity in polymerization and oligomerization of phenylacetylene (PhA) in THF and CH_2Cl_2. In THF, all the complexes provided high-molecular-weight poly(phenylacetylene) (PPhA) of M_w = (1.5–8.0) × 10^4 (Table II) with unimodal M_w distribution

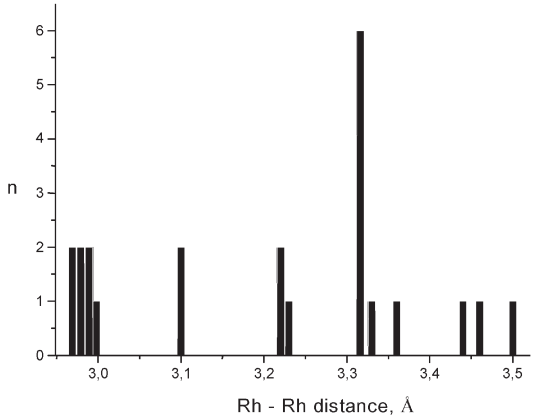


FIG. 7
Histogram of Rh(1)···Rh(2) distances found in Cambridge Crystallographic Data Centre for all compounds containing two Rh atoms bridged by at least one carboxylato ligand (*n*)

of the polymer fraction. ^{1}H NMR analysis confirmed the typical polyacetylene structure of PPhA consisting of polyvinylene main chain with pendant phenyls. The presence of a strong sharp signal of vinylic hydrogen at 5.95 ppm in ^{1}H NMR spectra ($CDCl_3$) proved predominantly *cis-transoid* configuration of PPhA. All polymerizations in THF were accompanied by a formation of methanol-soluble oligomeric products containing irregular *cis*/*trans* linear oligomers of PhA (M_w < 1000) and traces of cyclotrimers (1,2,4- and 1,3,5-triphenylbenzenes) as revealed by ^{1}H NMR. The overall yields of oligomers (Y_O) and PPhA (Y_P), and molecular weight characteristics of the PPhA achieved with individual complexes are summarized in Table II. The time course of polymerization with the most active complex

TABLE II

Yields of oligomers (Y_O) and polymer (Y_P), and weight-average (M_w) and number-average (M_n) molecular weights of polymers obtained in polymerization of phenylacetylene with Rh(I) complexes in THF and CH_2Cl_2 solvents (initial monomer concentration $[M]_0$ = 0.6 mol l^{-1}, initial monomer to Rh mole ratio $[M]_0/[Rh]$ = 200, room temperature, reaction time 420 min)

Entry	Rh complex	Solvent	Y_o, %	Y_P, %	$M_w \cdot 10^{-3}$	$M_n \cdot 10^{-3}$
1	**1a**	THF	7.0	16	68	28
2	**2a**	THF	16	21	51	20
3	**3a**	THF	14	15	15	7.2
4	**4a**	THF	22	20	61	19
5	**1b**	THF	21	29	23	9.0
6	**2b**	THF	25	25	80	27
7	**3b**	THF	23	23	31	14
8	**4b**	THF	21	23	27	12
9	**1a**	CH_2Cl_2	14	0		
10	**2a**	CH_2Cl_2	24	0		
11	**3a**	CH_2Cl_2	47	0		
12	**4a**	CH_2Cl_2	22	0		
13	**1b**	CH_2Cl_2	26	0		
14	**2b**	CH_2Cl_2	19	0		
15	**3b**	CH_2Cl_2	22	0		
16	**4b**	CH_2Cl_2	27	0		

1b is shown in Fig. 8. Polymerization was relatively rapid at the initial stage (~200 min); however, then it was slowed down and stopped before all the monomer was consumed. At a prolonged reaction time (24 h) the monomer conversion 60% and Y_P = 35% were only achieved (determined by SEC analysis). A slow decrease in molecular weight averages observed at the latter stage of reaction could reflect the lowered monomer concentration at that stage and, partly, also a degradation of the formed polymer[12]. As evident from Table II, no unambiguous relation between the composition of complexes and their activity in PhA polymerization has been found. Under the given conditions, the values of Y_P from 20 to 30% were achieved with complexes containing the nbd ligand (**1b**–**4b**) while slightly lower yields of PPhA (15–20%) resulted with their cod counterparts (**1a**–**4a**). Higher activity of nbd containing complexes as compared with their cod counterparts was reported for the [Rh(acac)(diene)] [13] (acac = acetylacetonato) and $[\{Rh(diene)\}_2(\mu\text{-}Cl)_2]$ [2] complexes.

In CH_2Cl_2, only a methanol-soluble oligomeric fraction (Y_O = 14–47%) resulted as the reaction product with all the complexes (Table II). This fraction always contained linear *cis*/*trans* oligomers (40–60% of the overall yield, by SEC analysis) and cyclotrimers (60–40% of the overall yield). From the reaction products obtained with **3a** (the highest Y_O value; Table II, entry 11) cyclotrimers were quantitatively isolated by column chromatogra-

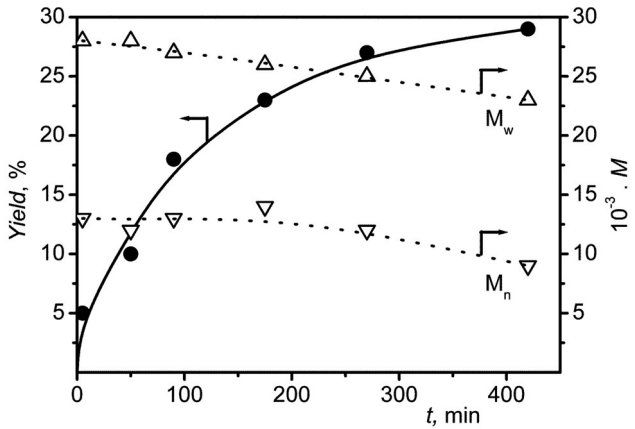


FIG. 8

Dependance of the yield (●), and M_n (▽) and M_w (△) values of PPhA in polymerization of PhA with **1b** in THF on reaction time (initial monomer concentration $[M]_0$ = 0.6 mol l^{-1}, initial monomer to Rh mole ratio $[M]_0/[Rh]$ = 200, room temperature)

phy on silica gel with hexane/CH_2Cl_2 9:1 (45% of the overall yield) and analysed by ^1H NMR. Their spectra were in qualitative accordance with those reported[14,15] for a mixture of 1,2,4- and 1,3,5-triphenylbenzenes. From the intensity of the signal at 7.80 ppm (central benzene ring protons of 1,3,5- isomer) and the intensity for all protons of both isomers, the molar ratio 1,2,4-triphenylbenzene/1,3,5-triphenylbenzene 90:10 was determined. Cyclotrimerization induced with the $[\{Rh(diene)\}_2(\mu\text{-}OCOR)_2]$ complexes will be investigated in more detail in the near future with the aim to optimize the reaction as far as higher cyclotrimerization yields and selectivity are concerned.

CONCLUSIONS

Dinuclear complexes $[\{Rh(cod)\}_2(\mu\text{-}OCOR)_2]$ and $[\{Rh(nbd)\}_2(\mu\text{-}OCOR)_2]$ with four diverse R groups were prepared by the ultrasound-assisted reaction of the $[\{Rh(cod)\}_2(\mu\text{-}Cl)_2]$ or $[\{Rh(nbd)\}_2(\mu\text{-}Cl)_2]$ complexes with the silver salts of carboxylic acids. Water was shown to be an appropriate reaction medium for obtaining complexes in desirable purity (free of polynuclear Rh species). All the complexes catalyze polymerization of phenylacetylene giving low to moderate yields of regular *cis-transoid* poly(phenylacetylene) and irregular linear oligomers in solvent as THF. When CH_2Cl_2 was used, all complexes showed only oligomerization activity giving mixtures of linear oligomers and cyclotrimers of phenylacetylene.

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