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Syntheses and structures of novel cyclic and dinuclear organorhodoximes: a homologous series of di- to penta-methylene-bridged complexes ‡

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The compound $[Rh(Hdmg)_2(PPh_3)]^-$ ($[Rh]^-$), synthesized by reduction of [Rh]–Cl with $NaBH_4$ in methanolic KOH, reacted with 1,2-disubstituted ethanes XCH_2CH_2X' (X/X′ = Cl/OMe or Br/Br) forming [Rh]–CH_2CH_2OMe **1a** as well as [Rh]–Br and ethylene as heterolytic fragmentation products. Heterolytic fragmentation of **1a** enforced by protonation with acids (CF_3SO_3H, CD_3CO_2D) generated MeOH, $H_2C{=}CH_2$ and [Rh]–O_3SCF_3 and [Rh]–O_2CCD_3, respectively. Reaction of $[Rh]^-$ with XCH_2CH_2X' (X/X′ = Cl/Cl, Cl/Br or Cl/OPh) afforded the dinuclear complex [Rh]CH_2CH_2[Rh] **2a**. The anion $[Rh]^-$ reacted with $Cl(CH_2)_3Cl$ to give [Rh]–$CH_2CH_2CH_2Cl$ **1b**, whereas $Br(CH_2)_3Br$ was reacted with excess and equimolar amounts of $[Rh]^-$, yielding [Rh]$CH_2CH_2CH_2$[Rh] **2b** and [Rh{$(CH_2)_3$ON=C(Me)C(Me)=NO}(Hdmg)(PPh_3)] **3b**, respectively. Similar reactions carried out with $Br(CH_2)_nBr$ (n = 4 or 5) yielded [Rh]–$(CH_2)_5Br$ **1d**, [Rh]$(CH_2)_n$[Rh] (n = 4 **2c** or 5 **2d**) and [Rh{$(CH_2)_n$ON=C(Me)C(Me)=NO}(Hdmg)(PPh_3)] (n = 4 **3c** or 5 **3d**), respectively. All complexes were fully characterized by NMR spectroscopy (^1H, ^{13}C, ^{31}P). The ^{31}P-{^1H} NMR spectra of dinuclear complexes **2a** and **2b** exhibit typical AA′ patterns of AA′XX′ systems (A = ^{31}P, X = ^{103}Rh) due to considerable $^5J(^{31}P–^{31}P)$ and $^6J(^{31}P–^{31}P)$ couplings (36.7, 11.2 Hz), respectively. The crystal structures of the dinuclear rhodoximes **2a**–**2c** and of the cyclic organorhodoxime **3b** have been determined. The two $(Hdmg)_2$ planes in the di- and tetra-methylene-bridged complexes **2a** and **2c** are parallel with distances of 4.5 (**2a**) and 7.1 Å (**2c**), respectively, and exhibit an ecliptic conformation. In the trimethylene-bridged complex **2b**, the two $(Hdmg)_2$ planes include an angle of 45.0(1)° and exhibit a staggered conformation, which minimizes electrostatic repulsion between the O–H–O moieties and the steric interference between two methyl groups. In all three complexes the oligo-methylene bridges are fully staggered. In **3b** the six-membered ring (1-oxa-2-aza-3-rhodacyclohexane) exhibits a distorted chair conformation. The distance between the two O atoms in the O–H–O bridge [O(2) · · · O(3) 2.58(1) Å] is distinctly shorter than those that are not connected *via* a hydrogen bridge [O(1) · · · O(4) 3.30(1) Å].

Hydrocarbon-bridged dinuclear complexes of transition metals can be considered as connections between mononuclear organometallic compounds and organometallic clusters and might be intermediates or model compounds in catalytic processes. Therefore, they have been the subject of intensive studies in the last years and reviews of salient aspects of these complexes have appeared.[1] In 1963 King[2] reported the first simple saturated hydrocarbon-bridged complexes of the type $M(CH_2)_nM'$ without metal–metal bonds or additional bridging ligands. Since then some complexes have been prepared with oligomethylene chains linking two L_xM centers using monodentate (like C_5H_5, CO, PR_3) or macrocyclic [like porphyrins, $(Hdmg)_2$ (H_2dmg = dimethylglyoxime)] ligands L. Only a few, having monodentate auxiliary ligands, have been structurally characterized.[3] The only example in the Cambridge Structural Database[4] where the metals have macrocyclic ligands is the tetramethylene-bridged vitamin B_{12} dimer.[5] Here we report the synthesis, reactivity, characterization and structures of organorhodoximes of the type [Rh]$(CH_2)_n$[Rh] with n = 2–5, a homologous series of di- to penta-methylene-bridged complexes.

Organorhodoximes [Rh$(Hdmg)_2$(L)R] (L = axial base), first prepared by Weber and Schrauzer,[6] have been extensively investigated. None but the triphenylphosphine derivatives (L = PPh_3) was synthesized with all basic types of hydrocarbyl ligands R (sp^3: alkyl; sp^2: vinyl, aryl, allenyl; sp: alkynyl) and with functionalized organo ligands such as $(CH_2)_nYR_x$ and $CH{=}CHYR_x$ (Y = element of Groups 15–17).[7] The electronic structure in the linear complex fragment P–Rh–C can be studied by NMR spectroscopy ($I = \frac{1}{2}$: ^{103}Rh, ^{31}P, ^{13}C).[8,9] The coupling constants $^1J(^{103}Rh–^{31}P)$ and bond lengths d(Rh–P) were used to study the NMR and structural *trans* influence of R.[9,10]

To date, many mononuclear organorhodoximes have been described,[7,11] but there is only one report of a dinuclear hydrocarbon-bridged rhodoxime, namely [{$K(MeOH)_2$}$_2$-{(Ph_3P)(dmg)(Hdmg)Rh–CH=CH–Rh(dmg)(Hdmg)(PPh_3)}], which was also structurally characterized.[12]

Furthermore, in organorhodoximes the pseudo-macrocyclic equatorial ligand, $(Hdmg)_2$, usually does not undergo reactions except for protonation/deprotonation or functionalization of the O–H–O groups.[13] Recently, reduction of an oxime to an imine group was observed upon reaction of $[Rh(Hdmg)_2]^-$ with phosphines.[14] Here, we also report unprecedented substitution reactions to give rhodacycles *via* ω-halogenoalkylrhodoximes as intermediates.

Experimental

All reactions with Rh^I were carried out under argon using Schlenk techniques. Solvents were dried and distilled under argon according to standard methods. The compound [Rh-$(Hdmg)_2(PPh_3)Cl$] ([Rh]–Cl) was prepared by a published method.[15] The other chemicals were commercial materials used without further purification.

Microanalyses (C, H, N, Cl, Br) were performed by the

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‡ Abbreviations: [Rh] = $[Rh(Hdmg)_2(PPh_3)]$, H_2dmg = dimethylglyoxime, R = hydrocarbyl ligand.

Table 1 Synthesis of organorhodoximes **1**–**3**

Compound	Yield (%)	$X(CH_2)_nX'$	*n*/mmol (t_{add}[a]/min)	t_{react}[a]/min	Solvent for recrystallization
1a	56	$Cl(CH_2)_2OMe$	2.00 (15)	>400[b]	CH_2Cl_2
1b	58	$Cl(CH_2)_3Cl$	2.00 (15)	60	Me_2CO
1d	40	$Br(CH_2)_5Br$	4.00 (<1)	1	$CHCl_3$
2a	44	$Br(CH_2)_2Cl$	1.52 (30)	60	
	18	$Cl(CH_2)_2OPh$	1.52 (30)	90	
	24	$Cl(CH_2)_2Cl$	1.52 (30)	120	
2b	51	$Br(CH_2)_3Br$	1.52 (15)	15	Me_2CO
2c	34	$Br(CH_2)_4Br$	1.52 (5)	5	$CHCl_3$
2d	67	$Br(CH_2)_5Br$	1.52 (30)	30	$CHCl_3$
3b	43	$Br(CH_2)_3Br$	2.00 (5)	5	CH_2Cl_2
3c	48	$Br(CH_2)_4Br$	2.00 (2)	2	Me_2CO
3d	5	$Br(CH_2)_5Br$	1.52 (5)	5	Me_2CO–Et_2O

[a] For definition see text; t_{react} includes t_{add}. [b] Stirring overnight.

University of Halle microanalytical laboratory using a CHNS-932 (LECO) and vario EL (elementar Analysensysteme) elemental analyser, respectively. The ^1H, ^{13}C and ^{31}P NMR spectra were obtained with Varian Unity 500 and Gemini 200 spectrometers (^1H at 499.88/199.97 MHz, ^{13}C at 125.71/50.289 MHz, ^{31}P at 80.95 MHz). Solvent signals (^1H, ^{13}C) were used as internal standards, $\delta(^{31}P)$ relative to external H_3PO_4 (85%). Heteronuclear multiple quantum correlation (HMQC) spectra were recorded on Varian Unity 500 spectrometer operating at 125.71 MHz for ^{13}C by ^1H observation. Thermoanalytic investigations were performed on a STA 409C (Netzsch) instrument in a helium atmosphere. A CP9000 (Chrompack) chromatograph was used for gas chromatographic analyses.

Preparations

[Rh]–$(CH_2)_2$OMe 1a, [Rh]–$(CH_2)_3$Cl 1b and [Rh]–$(CH_2)_5$Br 1d. To a solution of [Rh]–Cl (957 mg, 1.52 mmol) in methanolic KOH (75 cm^3, 0.15 M) was added dropwise a solution of $NaBH_4$ (76 mg, 2.00 mmol) in methanolic KOH (25 cm^3, 0.15 M) and stirred for 2 h at 20 °C to give a deep violet solution of $[Rh]^-$. To this a solution of $Cl(CH_2)_2OMe$, $Cl(CH_2)_3Cl$ or $Br(CH_2)_5Br$ (*n* mmol, see Table 1) in methanol (20 cm^3) was added within t_{add} (see Table 1). After the mixture had turned yellow (t_{react}, Table 1) stirring was continued for 30 min and water (100 cm^3) was added. In the case of compounds **1a** and **1b** the reaction mixture was neutralized (pH 7–8) with solid CO_2. After 12–24 h the yellow precipitate was filtered off, washed with diethyl ether (**1a**, **1d**) or ethanol (**1b**) and recrystallized.

Compound **1a**: m.p. 183–188 °C (decomp.) (Found: C, 53.4; H, 5.5; N, 8.3. $C_{29}H_{36}N_4O_5PRh$ requires C, 53.2; H, 5.5; N, 8.5%); δ_H(200 MHz, $CDCl_3$) 1.24 (2 H, m, α-CH_2), 1.80 [12 H, d, ^5J(PH) 2.15 Hz, 4 CH_3], 3.12 (2 H, m, β-CH_2), 3.12 (3 H, s, OCH_3) and 7.3 (15 H, m, 3 C_6H_5). Compound **1b**: m.p. 160–165 °C (decomp.) (Found: C, 51.6; H, 5.2; Cl, 5.2; N, 8.0. $C_{29}H_{35}ClN_4O_4PRh$ requires C, 49.2; H, 5.0; Cl, 5.0; N, 7.9%); δ_H(500 MHz, $CDCl_3$) 1.10 (2 H, m, α-CH_2), 1.39 (2 H, m, β-CH_2), 1.83 [12 H, d, ^5J(PH) 2.15, 4 CH_3], 3.25 [2 H, t, ^3J(HH) 7.23 Hz, γ-CH_2] and 7.3 (15 H, m, 3 C_6H_5). Compound **1d**: m.p. 145–147 °C (decomp.) (Found: C, 49.0; H, 5.4; Br, 11.3; N, 7.2. $C_{31}H_{39}BrN_4O_4PRh$ requires C, 49.9; H, 5.3; Br, 10.7; N, 7.5%); δ_H(500 MHz, $CDCl_3$) 0.99 (2 H, m, γ-CH_2), 1.18 (4 H, m, α-, β-CH_2), 1.69 [2 H, qnt, ^3J(HH) 7.30, δ-CH_2], 1.81 [12 H, d, ^5J(PH) 1.95, 4 CH_3], 3.25 [2 H, t, ^3J(HH) 7.03 Hz, ε-CH_2] and 7.3 (15 H, m, 3 C_6H_5).

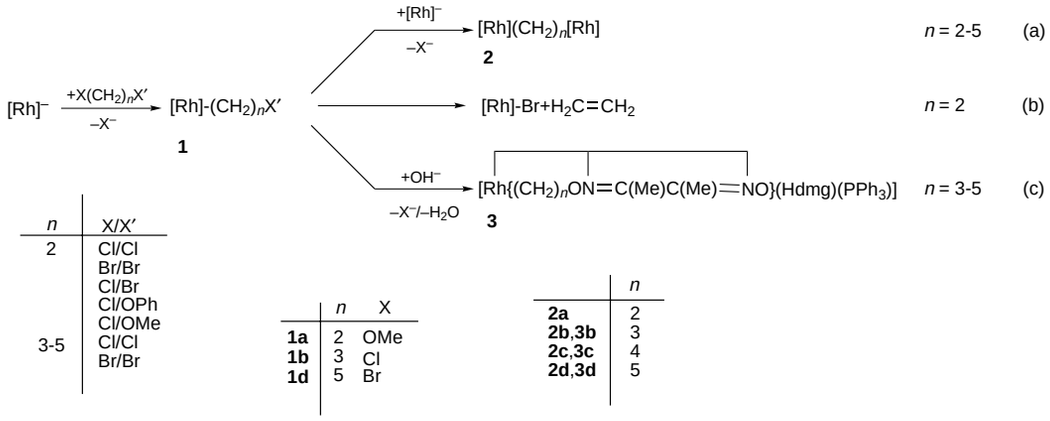
[Rh]$(CH_2)_n$[Rh] 2a–2d and [Rh{$(CH_2)_n$ON=C(Me)C(Me)=N-O}(Hdmg)(PPh_3)] 3b–3d. To a stirred solution of $[Rh]^-$ (1.52 mmol) in methanolic KOH (100 cm^3, 0.15 M), prepared as described above, was added within t_{add} (see Table 1) a solution of $X(CH_2)_nX$ (*n* mmol, see Table 1) in methanol (20 cm^3). After the mixture had turned yellow (t_{react}, Table 1), stirring was continued for 30 to 60 min and water (100 cm^3) was added. After 12–24 h the precipitate was filtered off. In the case of compound **2a**, without adding water, the precipitate was washed with acetone (2 × 10 cm^3) and dried *in vacuo*; for **2b**–**2d**, the yellow precipitate was thoroughly washed with acetone (**2b**) or diethyl ether (**2c**, **2d**) and recrystallized. In the case of **3b**, after addition of water, the reaction mixture was neutralized with solid CO_2 (pH 7–8). The precipitate was filtered off, washed with diethyl ether (2 × 5 cm^3) and recrystallized. For **3c** and **3d**, the precipitate was extracted three times with 10 cm^3 acetone (**3c**) or ether (**3d**). The extract was dried (Na_2SO_4) and concentrated. The orange precipitate was recrystallized (**3c**) and dissolved in acetone and reprecipitated with ether (three times) (**3d**).

Compound **2a**: T_{dec} 215–220 °C (Found: C, 52.9; H, 5.1; N, 9.0. $C_{54}H_{62}N_8O_8P_2Rh_2$ requires C, 53.2; H, 5.1; N, 9.2%); δ_H(200 MHz, $CDCl_3$–MeOH 15:1) 1.11 (4 H, m, 2 α-CH_2), 1.69 [24 H, d, ^5J(PH) 1.71 Hz, 8 CH_3] and 7.2 (30 H, m, 6 C_6H_5). Compound **2b**: T_{dec} 180–190 °C (Found: C, 53.3; H, 5.6; N, 9.2. $C_{55}H_{64}N_8O_8P_2Rh_2$ requires C, 53.6; H, 5.2; N, 9.1%); δ_H(200 MHz, $CDCl_3$) 0.58 (2 H, m, β-CH_2), 0.95 (4 H, m, 2 α-CH_2), 1.80 [24 H, d, ^5J(PH) 1.96 Hz, 8 CH_3] and 7.2 (30 H, m, 6 C_6H_5). Compound **2c**: T_{dec} 240–245 °C (Found: C, 52.6; H, 5.2; N, 8.6. $C_{56}H_{66}N_8O_8P_2Rh_2$ requires C, 53.9; H, 5.3; N, 9.0%); δ_H(200 MHz, $CDCl_3$) 0.71 (4 H, m, 2 β-CH_2), 1.07 (4 H, m, 2 α-CH_2), 1.76 [24 H, d, ^5J(PH) 2,15 Hz, 8 CH_3] and 7.2 (30 H, m, 6 C_6H_5). Compound **2d**: T_{dec} 205–210 °C (Found: C, 52.9; H, 5.7; N, 8.3. $C_{57}H_{68}N_8O_8P_2Rh_2$ requires C, 54.3; H, 5.4; N, 8.9%); δ_H(500 MHz, $CDCl_3$) 0.77 (4 H, m, 2 β-CH_2), 0.90 (2 H, m, γ-CH_2), 1.09 (4 H, m, 2 α-CH_2), 1.81 [24 H, d, ^5J(PH) 1.55 Hz, 8 CH_3] and 7.3 (30 H, m, 6 C_6H_5).

Compound **3b**: m.p. 170–172 °C (decomp.) (Found: C, 52.6; H, 5.3; N, 9.0. $C_{29}H_{34}N_4O_4PRh$ requires C, 54.7; H, 5.4; N, 8.8%); δ_H(500 MHz, $CDCl_3$) 1.25/1.49 (2 H, m, α-CH_2), 1.25/2.18 (2 H, m, β-CH_2), 3.82/5.08 (2 H, m, OCH_2), 1.49 (3 H, s, CH_3), 1.63 (3 H, s, CH_3), 1.79 [3 H, d, ^5J(PH) 2.35, CH_3], 2.07 [3 H, d, ^5J(PH) 2.78 Hz, CH_3] and 7.3 (15 H, m, 3 C_6H_5). Compound **3c**: m.p. 194–196 °C (decomp.) (Found: C, 55.0; H, 5.5; N, 8.4. $C_{30}H_{36}N_4O_4PRh$ requires C, 55.4; H, 5.6; N, 8.6%); δ_H(200 MHz, $CDCl_3$) 1.22/1.51/1.83/2.13 (6 H, 4 m, 3 CH_2), 1.51 [3 H, d, ^5J(PH) 1.18, CH_3], 1.65 [3 H, d, ^5J(PH) 1.60, CH_3], 1.79 [3 H, d, ^5J(PH) 2.34, CH_3], 2.00 [3 H, d, ^5J(PH) 2.58 Hz, CH_3], 4.15/6.45 (2 H, 2 m, OCH_2) and 7.3 (15 H, m, 3 C_6H_5). Compound **3d**: T_{dec} 215–220 °C; δ_H(200 MHz, $CDCl_3$) 0.8–2.3 (20 H, 4 CH_2 and 4 CH_3), 3.90/5.40 (2 H, 2 m, OCH_2) and 7.4 (15 H, m, 3 C_6H_5).

Reactions of [Rh]–CH_2CH_2OMe 1a with CF_3SO_3H and CD_3CO_2D

To a solution of compound **1a** (100 mg, 0,15 mmol) in $CDCl_3$ (0.7 cm^3) the appropriate amount of CF_3SO_3H and CD_3CO_2D, respectively, was added with a microsyringe. The reactions were



Scheme 1

monitored by NMR (^{1}H, ^{13}C) spectroscopy. Additionally, ethylene was identified by gas chromatography.

Thermolysis of [Rh](CH$_2$)$_n$[Rh] 2a–2d

In a sealed tube compound **2** (30–50 mg) was heated (*ca.* 4 K min^{-1}) to 250 °C. After 20 min the gaseous products were analysed by gas chromatography.

Crystallography

Suitable single crystals of compounds **2b**, **2c** and **3a** were obtained by recrystallization from the solvent given in Table 1; those of **2a** were grown directly in the reaction mixture. Compound **2c** was mounted in a glass capillary together with mother-liquor. The X-ray measurements were performed on a STOE-Stadi4 four-circle diffractometer (**2a**) and on a STOE IPDS image-plate system (**2b**, **2c**, **3b**), respectively. For **2a** the absorption correction was based on several ψ scans (T_{min}, T_{max} 0.83, 1.00). For all measurements on the image-plate system the reciprocal space was scanned with 133 frames for each of which the crystal was oscillated 1.5° around the φ axis; an absorption correction was carried out numerically.

Crystal data collection and processing parameters are listed in Table 2. The data were corrected for Lorentz-polarization and absorption; equivalent reflections were merged. The structures were solved with direct methods (SHELXS 86[16]) and subsequent Fourier-difference syntheses revealed the positions of all non-hydrogen atoms which were refined with anisotropic displacement parameters by full-matrix least-squares routines against F^2 (SHELXL 93[17]). Hydrogen atoms were placed in calculated positions and refined isotropically with fixed displacement parameters (riding model). The C_2 bridge in **2a** is disordered due to a location of atom C(27) in two positions with the same probability depicted with A and B. Residual electron densities in **2c** are considered to belong to a further solvate molecule which did not refine well and was hence omitted in the refinement.

CCDC reference number 186/789.

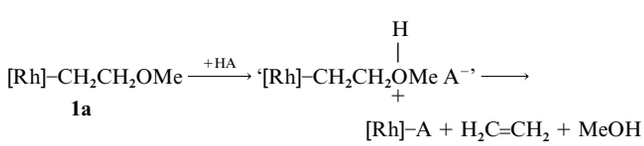
See http://www.rsc.org/suppdata/dt/1998/221/ for crystallographic files in .cif format.

Results and Discussion

Syntheses

(CH$_2$)$_2$ building block. Bis(dimethylglyoximato)(triphenylphosphine)rhodate(I), [Rh]$^-$, was prepared by reduction of [Rh]–Cl with $NaBH_4$ in methanolic KOH.[18] It reacts with 1,2-disubstituted ethanes XCH_2CH_2X' (X = Cl or Br; X′ = Cl, Br, OPh or OMe) according to Scheme 1. In all cases the first step seems to be a nucleophilic substitution reaction, which can be considered as an oxidative-addition, to give 2-functionalized ethyl complexes **1** as intermediates. With X′ = Cl or OPh a subsequent nucleophilic substitution reaction (oxidative addition) affords the dinuclear ethanediyl complex **2a**, see Scheme 1(a). With X′ = Br the intermediate **1** undergoes a heterolytic fragmentation reaction providing [Rh]–Br and ethylene [Scheme 1(b)].

The reaction of [Rh]$^-$ with $ClCH_2CH_2OMe$ yields [Rh]–CH_2-CH_2OMe **1a** as the main product. Complex **1a** is completely stable at room temperature, but with protonation it decomposes to give methanol and ethylene as a result of a heterolytic fragmentation, *cf.* Scheme 2. With CD_3CO_2D the reaction requires several days (**1a**:CD_3CO_2D = 1:3, $t_{\frac{1}{2}}$ *ca.* 7 d; **1a**:CD_3CO_2D = 1:8, $t_{\frac{1}{2}}$ *ca.* 2 d). Under the same conditions the ethyl complex [Rh]–CH_2CH_3 is completely stable and shows no Rh–C bond-splitting reaction. The strong acid CF_3SO_3H reacts with **1a** (**1a**:CF_3SO_3H = 1:1.5) at room temperature (r.t.) within a few minutes to give ethylene, methanol and [Rh]–O_3SCF_3 as heterolytic fragmentation products.



Scheme 2 HA = CF_3SO_3H or CD_3CO_2D

Obviously, the reactivity of complexes [Rh]–$(CH_2)_2X'$ strongly depends upon the nature of substituent X′: good nucleofugal leaving groups (Br^-, MeOH) induce heterolytic fragmentation and poor ones (MeO^-) lead to stable 2-functionalized ethyl complexes. An intermediate nucleophilicity of X′ (Cl^-, PhO^-) favours a nucleophilic substitution (oxidative-addition) reaction.

(CH$_2$)$_3$ building block. 1,3-Dichloropropane undergoes an oxidative-addition reaction with [Rh]$^-$ to give the 3-chloropropylrhodoxime **1b**, as the main product (58% yield), see Scheme 1. The analogous reaction with 1,3-dibromopropane in a molar ratio $c_{Rh}:c_{Br(CH_2)_3Br} = 2:1$ affords the dinuclear propanediyl-bridged complex **2b** (51% yield) and in a molar ratio $c_{Rh}:c_{Br(CH_2)_3Br} = 1:1$ the cyclic organorhodoxime **3b** (43% yield). It can be assumed that the 3-bromopropyl complex **1** (X′ = Br, *n* = 3) is an intermediate in these two reactions, see Scheme 1. Considering the greater stability of C–Cl bonds compared with C–Br bonds, it becomes clear that the 3-chloropropylrhodoxime **1a** is stable under ambient reaction conditions. However, the corresponding bromo derivative undergoes a subsequent reaction, either an intramolecular substitution of Br^- by the deprotonated dimethylglyoximate ligand to give **3b** or an intermolecular nucleophilic substitution with [Rh]$^-$ to give the dinuclear complex **2b**.

(CH$_2$)$_n$ (*n* = 4 or 5) building block. As with 1,3-dibromopropane, Br(CH$_2$)$_n$Br (*n* = 4 or 5) reacts with an excess of [Rh]$^-$

Table 2 Crystal data collection and processing parameters* for complexes **2a**–**2c** and **3b**

	2a	**2b**	**2c**	**3b**
Molecular formula	$C_{54}H_{62}N_8O_8P_2Rh_2$	$C_{55}H_{64}N_8O_8P_2Rh_2$	$C_{62}H_{72}Cl_{18}N_8O_8P_2Rh_2$	$C_{29}H_{34}N_4O_4PRh$
M	1218.84	1232.90	1963.14	636.48
Colour	Yellow	Yellow	Yellow	Orange
Size/mm	0.3 × 0.2 × 0.1	0.2 × 0.2 × 0.05	0.2 × 0.2 × 0.05	0.2 × 0.2 × 0.05
T/K	293	293	220(1)	293
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$I2/a$
a/Å	16.520(2)	12.405(3)	9.127(3)	15.298(2)
b/Å	9.931(2)	15.004(6)	14.238(3)	11.928(2)
c/Å	16.721(3)	16.292(4)	18.729(8)	33.903(5)
α/°		108.61(3)	111.90(4)	
β/°	100.28(1)	98.53(2)	93.02(4)	100.232(12)
γ/°		96.58(3)	99.67(3)	
U/Å^3	2699.2(7)	2799(2)	2208.4(12)	6088(2)
Z	2	2	1	8
D_c/g cm^{-3}	1.500	1.463	1.476	1.389
μ/mm^{-1}	0.732	0.707	1.004	0.652
F(000)	1252	1268	990	2624
θ Range/°	2.40–25.00	1.94–24.03	2.62–25.00	1.81–23.97
Reflections collected	8879	23437	15629	25709
Independent reflections	4737	8232	7335	4725
R_{int}	0.0427	0.0608	0.0954	0.1032
Reflections with $I > 2\sigma(I)$	3678	6784	6395	3410
Data, parameters	4732, 344	8232, 676	7335, 452	4725, 352
Final $R1$, $wR2$ [$I > 2\sigma(I)$]	0.0318, 0.0718	0.0359, 0.0868	0.0857. 0.2617	0.0649, 0.2063
all data	0.0515, 0.0836	0.0478, 0.0923	0.0931, 0.2708	0.0956, 0.2268
Goodness of fit (S)	1.111	1.054	1.128	1.116
Final $(\Delta/\sigma)_{max}$	0.000	−0.001	0.009	−0.001
Largest residual peaks/e Å^{-3}	0.456, −0.404	0.902, −0.739	4.440, −0.877	2.199, −0.509

* Details in common: Mo-Kα radiation ($\lambda_o = 0.710\ 73$ Å), $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$, $S = [\Sigma w(F_o^2 - F_c^2)^2/(N_{obs} - N_{param})]^{\frac{1}{2}}$ (based on all data).

($c_{Rh} : c_{Br(CH_2)_nBr} = 2:1$) to give the dinuclear butanediyl- and pentanediyl-bridged complexes [Rh]$(CH_2)_n$[Rh] **2c** and **2d**, respectively. The reactions of equimolar amounts yield the rhodacyclic complexes **3c** and **3d**. The 5-bromopentyl intermediate **1d** could be isolated in a good yield (40%) by fast mixing of [Rh]$^-$ with a large excess of 1,5-dibromopentane ($c_{Rh} : c_{Br(CH_2)_5Br} = 1:2.6$).

Properties and stability of complexes

In all the reactions mixtures of complexes are formed as was confirmed by NMR spectroscopy. The dinuclear complexes **2b**–**2d** and the cyclic organorhodoximes **3b**–**3d** especially are products of parallel reactions. Which of them is formed as main product is dependent mainly on the molar ratio $c_{Rh} : c_{X(CH_2)_nX}$ used and on the type of halide substituent X. By fractional crystallization of the raw products all complexes are affordable as pure substances except **3d**. Owing to its good solubility and the very low yield (5%), **3d** contains about 15% each of the bromopentyl complex **1d** and the dinuclear complex **2d**.

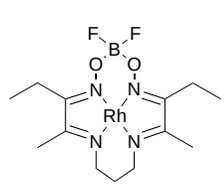
All complexes are stable in air and form yellow (**1a**, **1b**, **1d**, **2a**–**2d**, **3b**) and orange (**3c**, **3d**) crystals, respectively. The tetramethylene-bridged complex **2c** crystallizes as a solvate (**2c**·6$CHCl_3$) that rapidly loses chloroform in air. The identities of all complexes were confirmed by microanalysis and NMR spectroscopy as well as by crystal structure determinations for **2a**–**2c** and **3b**.

All complexes are thermally relatively stable. The dinuclear complexes **2a**–**2d** decompose between 180 and 245 °C without melting. Thus, the ethanediyl-bridged complex **2a** is stable in the solid state at 90 °C for at least 20 min. In $CDCl_3$: MeOH (15 : 1) at 50 °C a decomposition takes place to give ethylene and [Rh]–Cl within 1 h. The dimeric rhodium(II) complex [Rh]–[Rh] might be an intermediate that reacts rapidly with chloroform to give [Rh]–Cl as was shown in a separate experiment. Similarly, an equilibrium was found between LRh–CH_2CH_2–RhL [L = N_4 equatorial ligands like porphyrinate and 1,2-bis(pyridine-2-carboxamido)benzene derivatives] and LRh–RhL and ethylene.[19]

Thermolysis of the ethanediyl complex **2a** yields nearly exclusively ethylene and only small amounts of CH_4 (1%) and C_2H_6 (3%). In the case of **2b** the main product is propene; side products are cyclopropane (1%) and traces (Σ 0.4%) of CH_4, C_2H_6, C_2H_4 and C_3H_8. In contrast, thermolysis of the analogous cobaloxime [(py)$(Hdmg)_2Co(CH_2)_3Co(Hdmg)_2$(py)] (py = pyridine) affords only cyclopropane,[20] but there are conflicting reports on this complex (see below).

Thermolysis of the butane- and pentane-diyl complexes **2c** and **2d** is less selective. In the case of **2c** the main products are but-1-ene (60), buta-1,3-diene (20) and but-2-ene (8%) and in the case of **2d** pentenes (52%; pent-1-ene : pent-2-ene *ca.* 2 : 1) and penta-1,3-dienes (40%).

The neutral nucleophile [$Rh^{I}L'$] **A** reacts with 1,ω-dihalogeno-



A

alkanes to give mono- and di-nuclear complexes [Rh^{III}(L′)X-{$(CH_2)_nX'$}] and [X(L′)$Rh^{III}(CH_2)_nRh^{III}$(L′)X′] (n = 2, 3, 4, 6 or 10), respectively.[21] On the basis of kinetic studies, the authors assumed a 'not well understood' modest neighboring-group activation of bromine by the rhodium(III) macrocycle in the 2- and 3-bromoalkyl intermediates. Here, the kinetics of the corresponding reactions has not been investigated and qualitatively such effects have not been observed.

Analogous to the dinuclear rhodoximes **2**, the oligomethylene-bridged cobaloximes [(py)$(Hdmg)_2Co(CH_2)_nCo(Hdmg)_2$(py)] were prepared with n = 4–8.[22] However, there are

Table 3 Selected ^{1}H, ^{13}C and ^{31}P NMR data (δ, *J*/Hz) for type **1**–**3** complexes

	Hdmg		$(CH_2)_n$					PPh_3	
Complex	*C*=N	$CH_3(CH_3)$	α-*C* ($^{2}J_{PC}$, $^{1}J_{RhC}$)	β-*C* ($^{3}J_{PC}$)	γ-*C* ($^{4}J_{PC}$, $^{3}J_{RhC}$)	δ-*C*	ε-*C*	C_i[a] ($^{1}J_{PC}$, $^{2}J_{RhC}$)	*P* ($^{1}J_{RhP}$)
[Rh]–$(CH_2)_n$X									
1a X = OMe, *n* = 2	148.8	11.5 (1.80)	29.4 (77.1, 20.8)	72.9[b]				129.9 (30.8)	9.3 (64.7)
1b X = Cl, *n* = 3	148.7	11.6 (1.83)	29.1 (80.2, 20.8)	31.8 (3.1)	45.5 (16.2, 3.1)			130.1 (30.1)	9.4 (64.8)
1d X = Br, *n* = 5	148.2	11.5 (1.81)	34.2 (76.3, 20.0)	27.1 (3.8)	30.1 (11.6, 1.6)	32.4[c]	34.0[c]	130.3 (29.3)	8.9 (62.3)
[Rh]$(CH_2)_n$[Rh]									
2a *n* = 2	148.6	11.3 (1.69)	40.8[d] (66.6, 17.0)					130.0[d] (28.9, <1)	6.5[e] (65.0)
2b *n* = 3	148.4	11.6 (1.80)	36.7[d] (72.0, 19.4)	26.5[d] (<3)				130.5[d] (27.8, <1)	7.8[e] (61.8)
2c *n* = 4	148.3	11.5 (1.76)	35.4 (74.0, 20.0)	30.7 (11.6)				130.2 (27.4)	8.4 (59.8)
2d *n* = 5	148.3	11.5 (1.81)	35.8 (74.3, 19.4)	27.9	33.5 (10.9)			130.6 (27.9)	8.6 (61.0)
[Rh{$(CH_2)_n$ON=C(Me)C(Me)=NO}(Hdmg)(PPh_3)]									
3b *n* = 3	144.6[f]	11.2 (1.49)	25.5	26.6	79.4			130.3	14.7
	146.4	11.3 (1.63)	(73.8, 16.9)	(4.0)	(3.0)			(30.9)	(70.8)
	152.3[f]	12.3 (1.79[g])							
	167.1	14.0 (2.07[g])							
3c *n* = 4	144.5[f]	11.3 (1.51[g])	29.6	30.1[h]	29.9	73.5		130.6	13.1
	146.5	11.7 (1.65[g])	(75.5, 17.7)	(3.8)				(29.3)	(67.1)
	152.3	12.5 (1.79[g])							
	162.7	14.1 (2.00[g])							
3d *n* = 5	143.8[f]	11.1	33.1	30.2[h]	27.8[c]	25.0[c]	74.4	130.3	11.8
	147.9[f]	11.4	(67.0, 17.0)	(4.0)				(29.3)	(66.0)
	152.0	12.1							
	165.0	13.7							

[a] δ($^{13}C_o$) 133.2–133.8 [$^{2}J(^{31}P–^{13}C)$ = 10.8–12.0 Hz]; δ($^{13}C_m$) 127.6–128.1 [$^{3}J(^{31}P–^{13}C)$ = 8.5–9.3 Hz]; δ($^{13}C_p$) 129.5–129.9 [$^{4}J(^{31}P–^{13}C) \leqslant 2$ Hz]. [b] δ(CH_3) 57.6. [c] Assignments are uncertain. [d] A part of an AMM′XX′ system. [e] AA′ pattern of an AA′XX′ system. [f] $^{2}J(^{103}Rh–^{13}C)$ = 2.0–3.1 Hz, based on $^{13}C–\{^{31}P\}$ decoupling experiments. [g] $^{5}J(^{31}P–H)$ = 1.2–2.8 Hz. [h] Assignments are based on the magnitude of *J*(PC).

conflicting reports on the trimethylene-bridged cobaloxime (*n* = 3): the analogous synthesis failed, and attempts were unsuccessful[22] to prepare this complex as described in the literature.[20] To date, there have been no reports of the dimethylene-bridged cobaloxime (*n* = 2).

NMR spectroscopy

All compounds **1**–**3** were characterized by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy (see Table 3). The ^{31}P chemical shifts were found between δ 6.5 and 14.7 in the range expected for organorhodoximes with triphenylphosphine as axial base[7e] as is found generally for triphenylphosphine metal complexes.[23] For the dinuclear ethanediyl (**2a**) and propanediyl complexes (**2b**) the $^{31}P-\{^{1}H\}$ NMR spectra exhibit typical AA′ patterns of AA′XX′ systems (A = ^{31}P, X = ^{103}Rh). The simulations[24] of the observed spectra gave considerable $^{5}J(^{31}P–^{31}P)$ and $^{6}J(^{31}P–^{31}P)$ couplings (36.7, 11.2 Hz). The long-range Rh–P′ and Rh–Rh couplings are much smaller [**2a**, $^{4}J(^{103}Rh–^{31}P)$ = 4.4, $^{3}J(^{103}Rh–^{103}Rh) < 1$; **2b**, $^{5}J(^{103}Rh–^{31}P)$ = 1.1, $^{4}J(^{103}Rh–^{103}Rh) <$ 1 Hz]. For the homologous butanediyl- (**2c**) and pentanediyl-bridged (**2d**) complexes the corresponding coupling constants [$^{n}J(^{31}P–^{31}P)$, $^{n-1}J(^{103}Rh–^{31}P)$; *n* = 7 or 8] are zero and $^{31}P-\{^{1}H\}$ NMR spectra of first order were found.

The coupling constants $^{1}J(^{103}Rh–^{31}P)$ reflect the *trans* influence of the organo ligand R.[7e,g–i] Their magnitudes between 59.8 and 65.0 Hz for complexes **1** and **2** point to a *trans* influence of ω-halogenoalkyl [$(CH_2)_nX$] and metalloalkyl {$(CH_2)_n$[Rh]} ligands that is in the range of those for other alkyl and vinyl ligands (49–66 Hz), while the more electronegative alkynyl (*ca.* 80 Hz) and halide ligands (113–120 Hz) exhibit greater couplings, consistent with a weaker *trans* influence.

As expected for complexes **1**–**3**, the chemical shifts δ(^{13}C) of the aryl carbon atoms and the coupling constants $^{n}J(^{31}P–^{13}C)$ are in the order $\delta_o > \delta_i > \delta_p > \delta_m$ and $^{1}J \gg {}^{2}J \approx {}^{3}J > {}^{4}J$, respectively. Owing to the non-zero long-range couplings $^{5/6}J(^{31}P–^{31}P)$, $^{4/5}J(^{103}Rh–^{31}P)$, and $^{3/4}J(^{103}Rh–^{103}Rh)$ the carbon atoms C_i, C_o and C_m of **2a** and **2b** exhibit A parts of AMM′XX′ systems (A = ^{13}C, M = ^{31}P, X = ^{103}Rh) which could be simulated using the magnitudes of the coupling constants obtained from the ^{31}P NMR spectra (see Table 3 for C_i).

For the ω-halogenoalkyl complexes **1b** and **1d** the order of magnitude $^{2}J \gg {}^{4}J > {}^{3}J$§ of the coupling constants $^{n}J(^{31}P–^{13}C)$ was found. Furthermore, $^{1}J(^{103}Rh–^{13}C) \gg {}^{3}J(^{103}Rh–^{13}C)$ and $^{2}J(^{103}Rh–^{13}C) \approx 0$.

As a consequence of the long-range couplings between P and P′, Rh and Rh′, and Rh and P′, the resonances of the α-C atoms in the ethanediyl and propanediyl bridges of complexes **2a** and **2b** appear as the A parts of AMM′XX′ systems (A = ^{13}C, M = ^{31}P, X = ^{103}Rh). The experimental and simulated spectra for **2b** are shown in Fig. 1. In the case of the spin system of complex **2a**, a good correspondence between experimental and simulated spectra requires that at least one of the three long-range couplings has a negative sign. The central β-C atom of complex **2b** and all bridging carbon atoms of **2c** and **2d** exhibit first-order spectra.

§ The assignments of the carbon atoms were verified by H–C correlation spectroscopy (COSY). In the literature[7e] δ(^{13}C) of the β- and γ-carbon atoms in [Rh]–R (R = alkyl) were exchanged erroneously.

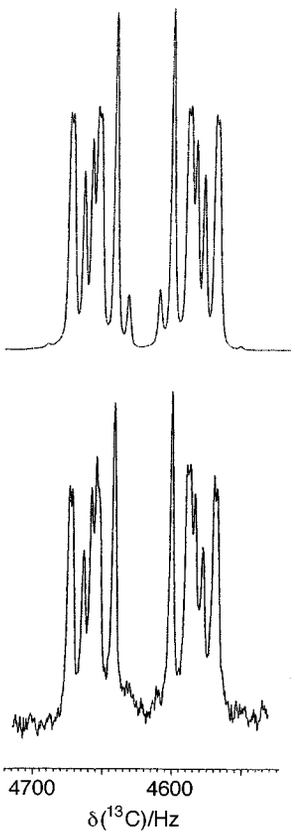


Fig. 1 Experimental (below) and simulated (above) ^{13}C NMR spectra of the α-C atom in complex **2b**. The coupling constants $^{1}J(Rh–P)$ = 61.8, $^{4}J(Rh–Rh) < 1$, $^{5}J(Rh–P) = 1.1$ and $^{6}J(P–P) = 11.2$ Hz were taken from the $^{31}P–\{^{1}H\}$ spectrum (see text and Table 3). The calculated coupling constants are as follows: $^{1}J(Rh–C) = 19.4$, $^{2}J(P–C) = 72.0$, $^{3}J(Rh–C) = 2.6$, $^{4}J(P–C) = 12.7$ and $^{5}J(Rh–P) = 2.6/3.0$ Hz

Owing to the formation of rhodacycles, all carbon atoms in complexes **3** are chemically inequivalent. Thus, the equatorial pseudo-macrocyclic ligand exhibits four signals for the C=N carbon atoms and four signals for the methyl carbon atoms (Table 3). In complexes **3b** and **3c** the carbon and proton resonances of the methyl groups were assigned on the basis of heteronuclear correlation (HETCOR) experiments.

In complexes **3** the carbon atoms attached to oxygen are shifted strongly downfield (73–79 ppm). All protons of the methylene groups $(CH_2)_n$ are chemically inequivalent and all geminal protons are well separated. Shift differences between geminal protons were found up to 1.26 ppm (γ-CH_2 in **3b**) corresponding to 630 Hz at 500 MHz. Thus, the proton resonances of the $(CH_2)_n$ groups appear as first-order multiplets in most cases.

Molecular structures

[Rh](CH$_2$)$_n$[Rh] (n = 2 2a, 3 2b or 4 2c). All complexes crystallize with discrete molecules without any remarkable intermolecular interactions. The molecular structures are shown in Figs. 2–4. Selected bond lengths and angles are listed in Tables 4–6. Complexes **2a** and **2c** have crystallographically imposed inversion symmetry.

The Rh atoms display a distorted octahedral co-ordination, with the two dimethylglyoximate ligands in the equatorial plane and PPh_3 and the alkanediyl ligand in the axial positions. As in other rhodoximes,[7,10,11] the two $Hdmg^-$ ligands are stabilized by two strong intramolecular O–H–O hydrogen bonds [O···O: **2a**, 2.694(4), 2.731(4); **2b**, 2.605(4)–2.782(4); **2c**, 2.694(8), 2.748(9) Å].

The P–Rh–C units are nearly linear (see Table 7). The Rh–P bond lengths [**2a**, 2.4755(9); **2b**, Rh(1)–P(1) 2.489(1), Rh(2)–P(2) 2.479(1); **2c**, Rh–P 2.484(2) Å] are in the range of those of analogous mononuclear alkylrhodoximes {[Rh]–R, R = Me, Et, Pr^i or Bu^t; Rh–P 2.454(1)–2.492(1) Å [10a,d–f]}. In the same way, the Rh–C bond lengths [**2a**, Rh–C(27A) 2.17(1), Rh–C(27B) 2.15(2); **2b**, Rh(1)–C(53) 2.118(3), Rh(2)–C(55) 2.120(3); **2c**, Rh–C(27) 2.117(7) Å] correspond to those in the mononuclear alkyl complexes [Rh]–R [R = Me, Et, Pr^i or Bu^t; Rh–C 2.064(7)–2.216(3) Å [10a,d–f]]. The two $Hdmg^-$ ligands are tilted away from the triphenylphosphine ligand as described by the angle (α)[25] between the normals to the Hdmg planes and by the displacement of the Rh atom out of the mean plane passing through the four oxime N-donor atoms toward the P atom [d(Rh/N$_4$)],[25] see Table 7. Similar values for α and d were found in mononuclear alkylrhodoximes (Table 7).

In complex **2b** the torsion angles Rh(1)–C(53)–C(54)–C(55) [179.2(3)] and C(53)–C(54)–C(55)–Rh(2) [174.5(3)°] reveal that the conformation of the $RhCH_2CH_2CH_2Rh$ chain is fully staggered (*ap*). Thus, both disc-like Rh(Hdmg)$_2$ moieties take up the greatest distance from each other. The tilt angle between the two N_4 planes is 45.0(1)°. These two planes exhibit a nearly perfectly staggered conformation [mean of the torsion angles N–Rh(1)–Rh(2)–N is 90.6°], which obviously minimizes the electrostatic repulsion between the O–H–O moieties and the steric interference between two methyl groups. The closest contacts between the two equatorial ligands [O(1)···C(16) 3.485(6); O(8)···C(1) 3.513(6) Å] correspond with the sum of van der Waals radii (3.50 Å) for a methyl group [$r_{vdW}(CH_3) = 2.00$ Å [26]] and an oxygen atom [$r_{vdW}(O) = 1.50$ Å].[26] The dimeric rhodium(II) complex [Rh]–[Rh] with its Rh–Rh single bond also exhibits a staggered conformation of the two (Hdmg)$_2$ ligands (deviation of the ideal conformation: 3.0°) with Me···O distances of 3.37 Å (mean value).[27]

The relatively large angles [Rh(1)–C(53)–C(54) 119.3(2), Rh(2)–C(55)–C(54) 118.3(2)°] seem not to be a consequence of the steric interference of the two (Hdmg)$_2$ moieties. Similar values were found in complex **2c** [Rh–C(27)–C(28) 119.9(5)°] and in the mononuclear rhodoximes [Rh]–R [R = Et or Pr^i: 116.2(5)–119.3(6)° [10a,e]].

As in complex **2b**, the conformations of the chains $RhCH_2$-CH_2Rh in **2a** and $RhCH_2CH_2CH_2CH_2Rh$ in **2c** are fully staggered (*ap*) [torsion angles: **2a**, Rh–C(27)–C(27′)–Rh 180; **2c**, Rh–C(27)–C(28)–C(28′) 177.1(7)°, C(27)–C(28)–C(28′)–C(27′) 180°]. As a consequence of the inversion centres, the two N_4 planes are parallel in **2a** and **2c** with distances of 4.5 (**2a**) and 7.1 Å (**2c**). Furthermore, the two RhN_4 units in **2a** and in **2c** exhibit a perfectly ecliptic conformation, contrary to the staggered conformation in **2b**.

Cyclic organorhodoxime 3b. Complex **3b** crystallizes with discrete molecules, see Fig. 5. Selected bond lengths and angles are listed in Table 8. The distortion of the co-ordination polyhedron RhN_4PC is similar to those of the dinuclear complexes **2** and other organorhodoximes (Table 7).

The six-membered ring (1-oxa-2-aza-3-rhodacyclohexane) exhibits a distorted chair conformation with angles between 79.7(3) [C(27)–Rh–N(1)] and 123.2(5)° [Rh–N(1)–O(1)] and torsion angles (absolute values) between 53.4(7) and 74.9(8)°. The relatively small angle C(27)–Rh–N(1) [79.7(3)°] compared with the other C–Rh–N angles [88.0(3)–91.7(3)°] might be indicative of a degree of strain in the ring as is the relatively large angle P–Rh–N(1) [97.4(2)°] compared with the other P–Rh–N angles [87.0(2)–94.0(2)°].

The N(1)–O(1) bond [1.424(9) Å] is significantly longer than the other N–O bonds [1.303(9)–1.380(9) Å]. In marked contrast to the O(2)–H(3)–O(3) unit [O(2)···O(3) 2.58(1) Å], the distance between the oxygen atoms that are not connected *via* a hydrogen bridge is distinctly longer [O(1)···O(4) 3.30(1) Å]. Correspondingly, the angle N(1)–Rh–N(4) [108.8(3) Å] is larger than N(2)–Rh–N(3) 98.1(3) Å.

To summarize, the reactions of $[Rh]^-$ with $X(CH_2)_nX'$ (n =

Table 4 Selected bond lengths (Å) and angles (°) for complex **2a**

Rh–P	2.4755(9)	C(27)–C(27′)[b]	1.44(3), 1.50(3)
Rh–C(27)[a]	2.17(1), 2.15(2)		
P–Rh–C(27)[a]	171.2(3), 172.3(3)	N(3)–Rh–N(4)	78.3(1)
Rh–C(27)–C(27′)[a]	116(1), 117(1)	N(1)–Rh–N(4)	100.6(1)
N(1)–Rh–N(2)	78.4(1)	N(2)–Rh–N(3)	101.7(1)
Mean values[b]			
Rh–N	1.988(16) [1.970(3), 1.999(3)]	C(27)–Rh–N[c]	86.1(59) [80.4(4), 92.6(4)]
N–O	1.344(32) [1.316(3), 1.375(4)]	P–Rh–N	93.8(10) [92.48(7), 94.59(8)]
P–C	1.831(4) [1.827(4), 1.837(4)]	C–P–C	102.7(22) [101.3(2), 105.4(2)]

Symmetry transformation (′): $-x, -y, -z$. [a] The first value refers to C(27A) and the second to C(27B). [b] σ_{n-1} in parentheses; minimum and maximum values in square brackets. [c] Values given for C(27A); for C(27B) 86.2(61) [79.1(4), 92.7(4)].

Table 5 Selected bond lengths (Å) and angles (°) for complex **2b**

Rh(1)–P(1)	2.489(1)	Rh(2)–C(55)	2.120(3)
Rh(2)–P(2)	2.479(1)	C(53)–C(54)	1.507(5)
Rh(1)–C(53)	2.118(3)	C(54)–C(55)	1.512(5)
P(1)–Rh(1)–C(53)	172.8(1)	N(1)–Rh(1)–N(4)	101.2(1)
P(2)–Rh(2)–C(55)	175.62(9)	N(2)–Rh(1)–N(3)	101.0(1)
Rh(1)–C(53)–C(54)	119.3(2)	N(5)–Rh(2)–N(6)	79.1(1)
Rh(2)–C(55)–C(54)	118.4(2)	N(7)–Rh(2)–N(8)	77.6(1)
C(53)–C(54)–C(55)	111.5(3)	N(5)–Rh(2)–N(8)	100.0(1)
N(1)–Rh(1)–N(2)	78.4(1)	N(6)–Rh(2)–N(7)	102.7(1)
N(3)–Rh(1)–N(4)	78.7(1)		
Mean values[a]			
Rh(1)–N	1.985(6) [1.977(3), 1.991(3)]	C(53)–Rh(1)–N	86.8(29) [83.2(1), 90.2(1)]
Rh(2)–N	1.989(9) [1.974(3), 1.995(3)]	C(55)–Rh(2)–N	87.3(45) [82.7(1), 93.0(1)]
N–O[b]	1.345(6) [1.340(4), 1.353(4)]	P(1)–Rh(1)–N	93.2(27) [90.01(9), 96.55(9)]
N–O[c]	1.352(21) [1.332(4), 1.380(4)]	P(2)–Rh(2)–N	92.8(24) [90.76(9), 96.18(9)]
P(1)–C	1.833(5) [1.828(4), 1.836(4)]	C–P(1)–C	102.8(41) [99.0(2), 107.0(2)]
P(2)–C	1.835(9) [1.828(4), 1.842(4)]	C–P(2)–C	103.6(30) [101.4(2), 107.1(2)]

[a] σ_{n-1} in parentheses; minimum and maximum values in square brackets. [b] Rh(1)(Hdmg)$_2$. [c] Rh(2)(Hdmg)$_2$.

Table 6 Selected bond lengths (Å) and angles (°) for complex **2c**

Rh–P	2.484(2)	C(27)–C(28)	1.50(1)
Rh–C(27)	2.117(7)	C(28)–C(28′)	1.53(1)
P–Rh–C(27)	176.6(2)	N(3)–Rh–N(4)	78.5(3)
Rh–C(27)–C(28)	119.9(5)	N(1)–Rh–N(3)	100.8(3)
C(27)–C(28)–C(28′)	112.9(8)	N(2)–Rh–N(4)	102.1(3)
N(1)–Rh–N(2)	78.2(3)		
Mean values*			
Rh–N	1.993(18) [1.972(7), 2.013(6)]	C(27)–Rh–N	87.5(24) [84.5(3), 90.0(3)]
N–O	1.359(24) [1.330(8), 1.379(8)]	P–Rh–N	92.6(20) [89.9(2), 94.7(2)]
P–C	1.834(15) [1.817(8), 1.846(7)]	C–P–C	103.4(31) [101.0(3), 106.9(3)]

Symmetry transformation (′): $-x + 1, -y + 1, -z + 1$. * σ_{n-1} in parentheses; minimum and maximum values in square brackets.

2–5) afford in the first step ω-halogenoalkyl rhodoximes **1** that can react further (i) with $[Rh]^-$ in an intermolecular reaction to give dinuclear oligo-methylene-bridged rhodoximes **2**, (ii) in an intramolecular substitution reaction to give cyclic organorhodoximes **3** ($n = 3$–5) or (iii) in a heterolytic fragmentation reaction with splitting off of ethylene ($n = 2$). The fully staggered conformation (*ap*) of the Rh(CH$_2$)$_n$Rh chains ($n = 2$–4) sufficiently prevents steric interference between the bulky disc-like pseudo-macrocyclic (Hdmg)$_2$ ligands, even in the propanediyl complex **2b**. (Difficulties in preparing the corresponding organocobaloxime were attributed to steric factors.[22]) These investigations contribute to the understanding of the stability

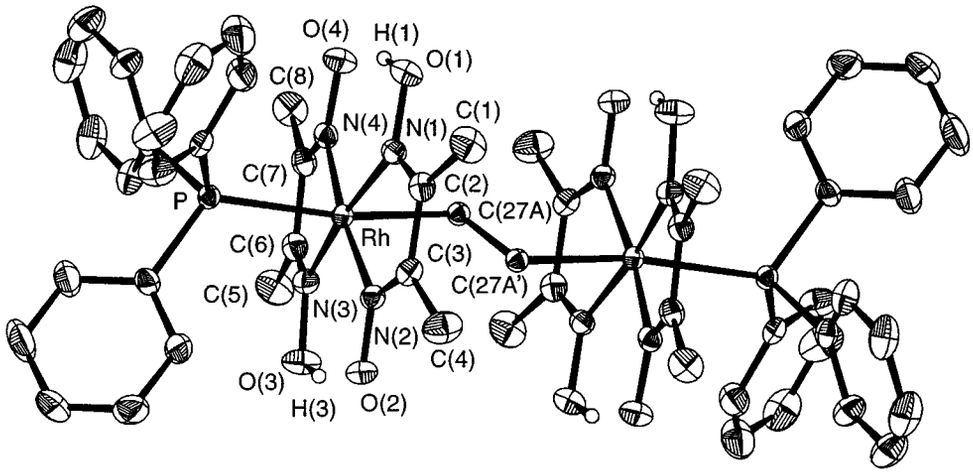


Fig. 2 Molecular structure and numbering scheme of complex **2a** [only split position C(27A) is shown]. Ellipsoids are drawn at the 30% probability level. Apart from the O–H–O bridges, hydrogen atoms have been omitted for clarity. For the same reason, phenyl carbons were not included in the numbering scheme

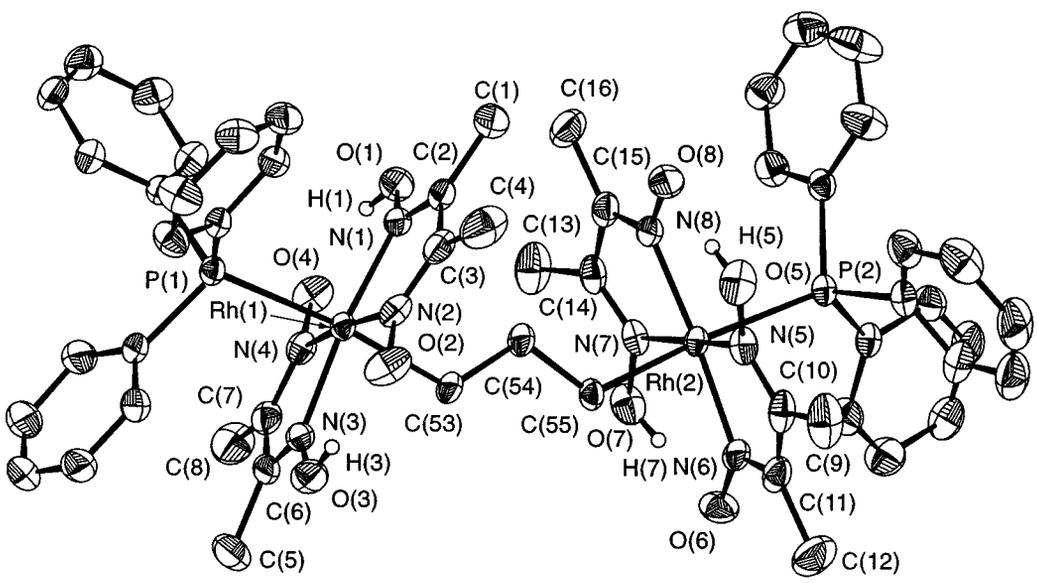


Fig. 3 Molecular structure and numbering scheme of complex **2b**. Details as in Fig. 2

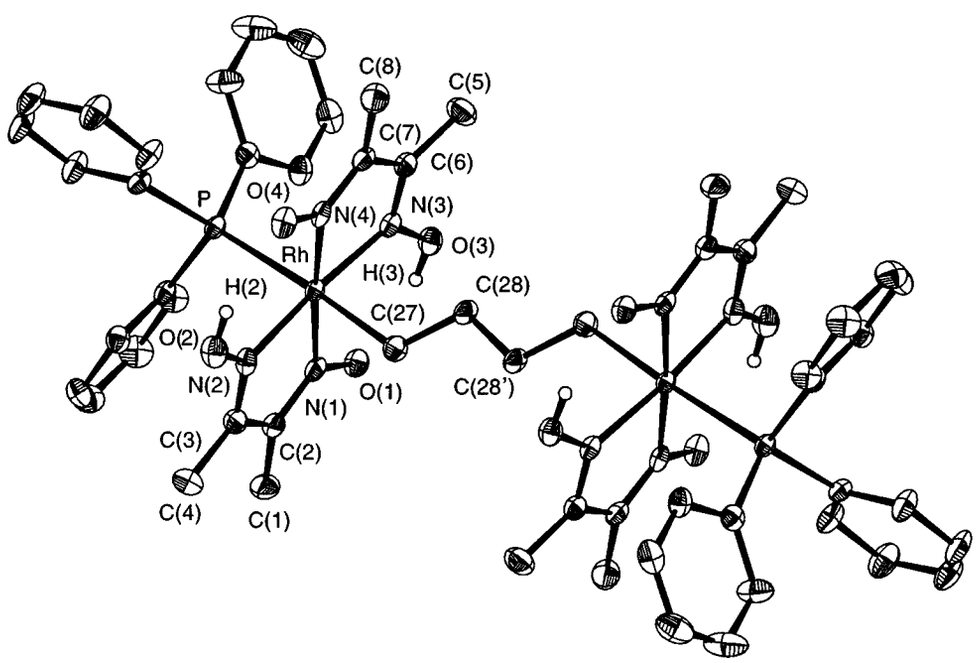


Fig. 4 Molecular structure and numbering scheme of complex **2c**·6$CHCl_3$. Solvent molecules are omitted. Details as in Fig. 2

Table 7 Structural parameters for the distortion of the co-ordination polyhedra RhN_4PC

Complex	α[a]/°	d(Rh/N_4)[a]/Å	P–Rh–C/°
2a	14.7(1)	0.133(1)	171.2(3), 172.3(3)[b]
2b[c]	8.4(2), 5.6(2)	0.111(1), 0.098(1)	172.8(1), 175.62(9)
2c	2.9(4)	0.088(3)	176.6(2)
3b	9.7(5)	0.089(4)	173.1(3)
[Rh]–R[d]	11.1	0.101	175.2
	[9.5(4)–13.5(5)]	[0.048(1)–0.130(1)]	[173.6(2)–177.0(1)]

[a] For definition of α and d see text. [b] First value refers to C(27A) and the second to C(27B). [c] First values refer to the Rh(1) centre and the second to Rh(2). [d] R = Me, Et, Pr^i or Bu^t;[10a,d–f] mean values are given with the range in square brackets.

Table 8 Selected bond lengths (Å) and angles (°) for complex **3b**

Rh–P	2.481(2)	P–Rh–C(27)	173.1(3)
Rh–C(27)	2.120(9)	Rh–C(27)–C(28)	111.0(7)
C(27)–C(28)	1.56(1)	C(27)–C(28)–C(29)	116.6(8)
C(28)–C(29)	1.51(1)	C(28)–C(29)–O(1)	113.8(8)
C(29)–O(1)	1.47(1)	Rh–N(1)–O(1)	123.2(5)
Rh–N(1)	2.022(7)	N(1)–Rh–C(27)	79.7(3)
Rh–N(2)	2.016(8)	N(1)–Rh–N(2)	75.7(3)
Rh–N(3)	1.989(7)	N(3)–Rh–N(4)	77.2(3)
Rh–N(4)	2.044(7)	N(1)–Rh–N(4)	108.8(3)
N(1)–O(1)	1.424(9)	N(2)–Rh–N(3)	98.1(3)
N(2)–O(2)	1.339(9)	P–Rh–N(1)	97.4(2)
N(3)–O(3)	1.380(9)	P–Rh–N(2)	94.0(2)
N(4)–O(4)	1.303(9)	P–Rh–N(3)	91.8(2)
		P–Rh–N(4)	87.0(2)

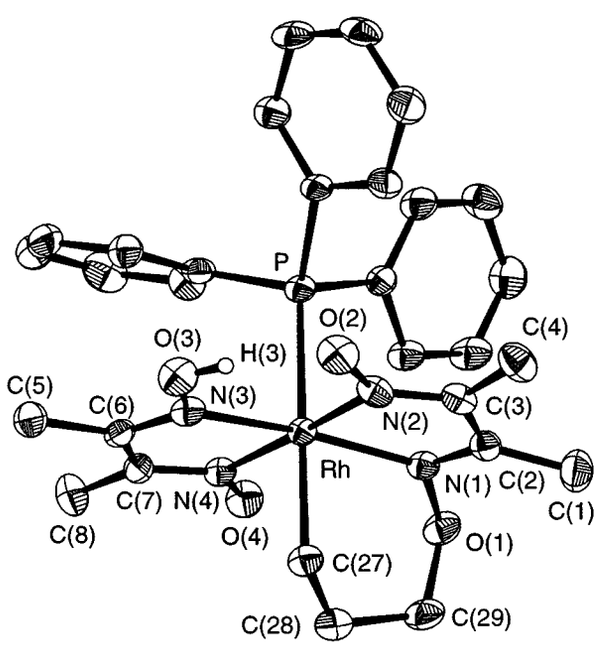


Fig. 5 Molecular structure and numbering scheme of complex **3b**. Details as in Fig. 2

and reactivity of oligo-methylene-bridged rhodoximes and reveal a novel pathway for an interligand reaction between an axial functionalized organo ligand and an equatorial oximato/oxime ligand.

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References

1 J. R. Moss and L. G. Scott, *Coord. Chem. Rev.*, 1984, **60**, 171; C. P. Casey and J. D. Audett, *Chem. Rev.*, 1986, **86**, 339; J. R. Puddephatt, *Polyhedron*, 1988, **7**, 767; W. Beck, B. Niemer and M. Wieser, *Angew. Chem.*, 1993, **105**, 969; *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 923.
2 R. B. King, *Inorg. Chem.*, 1963, **2**, 531.
3 Y. C. Lin, J. C. Calabrese and S. S. Wreford, *J. Am. Chem. Soc.*, 1983, **105**, 1679; D. J. Crowther, N. C. Baenziger and R. F. Jordan, *J. Am. Chem. Soc.*, 1991, **113**, 1455; F. R. Lemke, D. J. Szalda and R. M. Bullock, *J. Am. Chem. Soc.*, 1991, **113**, 8466; M. A. Gafoor, A. T. Hutton and J. R. Moss, *J. Organomet. Chem.*, 1996, **510**, 233; K. Raab, U. Nagel and W. Beck, *Z. Naturforsch., Teil B*, 1983, **38**, 1466; L. Pope, P. Sommerville, M. Laing, K. J. Hindson and J. R. Moss, *J. Organomet. Chem.*, 1976, **112**, 309; H. Adams, N. A. Bailey and M. J. Winter, *J. Chem. Soc., Dalton Trans.*, 1984, 273; K. P. Finch, J. R. Moss and M. L. Niven, *Inorg. Chim. Acta*, 1989, **166**, 181; S. J. Archer, K. P. Finch, H. B. Friedrich, J. R. Moss and A. M. Crouch, *Inorg. Chim. Acta*, 1991, **182**, 145.
4 Cambridge Structural Database (CSD), Cambridge Crystallographic Data Centre, University Chemical Laboratory, Cambridge.
5 B. Kräutler, T. Derer, P. Liu, W. Mühlecker, M. Puchberger, K. Gruber and C. Kratky, *Angew. Chem.*, 1995, **107**, 66; *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 84.
6 J. H. Weber and G. N. Schrauzer, *J. Am. Chem. Soc.*, 1970, **92**, 726.
7 (*a*) C. W. Fong and M. D. Johnson, *J. Chem. Soc., Perkin Trans. 2*, 1973, 986; (*b*) R. Dreos Garlatti, G. Tauzher and G. Costa, *Inorg. Chim. Acta*, 1986, **121**, 27; (*c*) K. R. Howes, A. Bakac and J. H. Espenson, *Inorg. Chem.*, 1988, **27**, 3147; (*d*) D. Steinborn, U. Sedlak and M. Dargatz, *J. Organomet. Chem.*, 1991, **415**, 407; (*e*) D. Steinborn and M. Ludwig, *J. Organomet. Chem.*, 1993, **463**, 65; (*f*) F. Asaro, R. Dreos Garlatti, G. Pellizer and G. Tauzher, *Inorg. Chim. Acta*, 1993, **211**, 27; (*g*) R. Boca, M. Dunaj-Jurco, I. Potocnak, D. Steinborn and M. Ludwig, *J. Mol. Catal.*, 1995, **95**, 141; (*h*) D. Steinborn, L. Yang and A. M. A. Aisa, *J. Organomet. Chem.*, 1996, **526**, 43; (*i*) A. M. A. Aisa, F. W. Heinemann and D. Steinborn, *Z. Anorg. Allg. Chem.*, 1996, **622**, 1946; (*j*) F. W. Heinemann, A. M. A. Aisa and D. Steinborn, *Z. Kristallogr.*, 1996, **211**, 837.
8 F. Asaro, G. Costa, R. Dreos, G. Pellizer and W. von Philipsborn, *J. Organomet. Chem.*, 1996, **513**, 193.
9 M. Ludwig, L. Öhrström and D. Steinborn, *J. Magn. Reson.*, 1995, **33**, 984.
10 (*a*) V. Kettmann, M. Dunaj-Jurco, D. Steinborn and M. Ludwig, *Acta Crystallogr., Sect. C*, 1994, **50**, 1239; (*b*) M. Dunaj-Jurco, V. Kettmann, D. Steinborn and M. Ludwig, *Acta Crystallogr., Sect. C*, 1994, **50**, 1427; (*c*) M. Dunaj-Jurco, V. Kettmann, D. Steinborn and M. Ludwig, *Acta Crystallogr., Sect. C*, 1995, **51**, 210; (*d*) I. Potocnak, M. Dunaj-Jurco, M. Ludwig and D. Steinborn, *Acta Crystallogr., Sect. C*, 1995, **51**, 1999; (*e*) M. Dunaj-Jurco, D. Miklos, I. Potocnak, M. Ludwig and D. Steinborn, *Acta Crystallogr., Sect. C*, 1996, **52**, 315; (*f*) V. Kettmann, M. Dunaj-Jurco, D. Steinborn and M. Ludwig, *Acta Crystallogr., Sect. C*, 1996, **52**, 1399.
11 N. Bresciani Pahor, R. Dreos-Garlatti, S. Geremia, L. Randaccio, G. Tauzher and E. Zangrando, *Inorg. Chem.*, 1990, **29**, 3437; B. Giese, J. Hartung, C. Kesselheim, H. J. Lindner and I. Svoboda, *Chem. Ber.*, 1993, **126**, 1193; S. Geremia, L. Randaccio, R. Dreos and G. Tauzher, *Gazz. Chim. Ital.*, 1995, **125**, 95; S. Geremia, R. Dreos, L. Randaccio, G. Tauzher and L. Antolini, *Inorg. Chim. Acta*, 1994, **216**, 125.
12 D. Steinborn, A. M. A. Aisa, F. W. Heinemann and S. Lehmann, *J. Organomet. Chem.*, 1997, **527**, 239.
13 R. Dreos Garlatti, G. Tauzher, M. Blaschich and G. Costa, *Inorg. Chim. Acta*, 1985, **105**, 129; J. H. Espenson and R. C. McHatton, *Inorg. Chem.*, 1981, **20**, 3090; F. Asaro, R. Dreos, S. Geremia, G. Nardin, G. Pellizer, L. Randaccio, G. Tauzher and S. Vuano, *J. Organomet. Chem.*, 1996, **525**, 71
14 R. Dreos, G. Tauzher, S. Geremia, L. Randaccio, F. Asaro, G. Pellizer, C. Tavagnacco and G. Costa, *Inorg. Chem.*, 1994, **33**, 5404.
15 P. Powell, *J. Chem. Soc. A*, 1969, 2418.
16 G. M. Sheldrick, SHELXS 86, Program for the Solution of Crystal Structures, University of Göttingen, 1986.
17 G. M. Sheldrick, SHELXL 93, Program for the Refinement of Crystal Structures, University of Göttingen, 1993.
18 T. Ramasami and J. H. Espenson, *Inorg. Chem.*, 1980, **19**, 1846.
19 Y. Ni, J. P. Fitzgerald, P. Carroll and B. B. Wayland, *Inorg. Chem.*, 1994, **33**, 2029; K. J. Del Rossi, X.-X. Zhang and B. B. Wayland, *J. Organomet. Chem.*, 1995, **504**, 47; M. Wei and B. B. Wayland, *Organometallics*, 1996, **15**, 4681.

20 G. N. Schrauzer and R. J. Windgassen, *J. Am. Chem. Soc.*, 1966, **88**, 3738.
21 J. P. Collman and M. R. MacLaury, *J. Am. Chem. Soc.*, 1974, **96**, 3019; J. P. Collman, J. I. Brauman and A. M. Madonik, *Organometallics*,1986, **5**, 218.
22 K. P. Finch and J. R. Moss, *J. Organomet. Chem.*, 1988, **346**, 253.
23 P. S. Pregosin and R. W. Kunz, *NMR basic principles and progress*, Springer, Berlin, 1979, vol. 16.
24 PERCH, an integrated software for analysis of NMR spectra on a personal computer, version 1/96, University of Kuopio, 1996.
25 N. Bresciani Pahor, M. Forcolin, L. G. Marzilli, L. Randaccio, M. F. Summers and P. J. Toscano, *Coord. Chem. Rev.*, 1985, **63**, 1; L. Randaccio, N. Bresciani Pahor and E. Zangrando, *Chem. Soc. Rev.*, 1989, **18**, 225.
26 J. E. Huheey, E. A. Keiter and R. L. Keiter, *Inorganic Chemistry: Principles of Structure and Reactivity*, Harper Collins, New York, 4th edn., 1993, p. 292.
27 K. G. Caulton and F. A. Cotton, *J. Am. Chem. Soc.*, 1971, **93**, 1914.

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