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Synthesis and structure of a μ-(*E*)-vinylene-bis[dimethylglyoximato(1-)-dimethylglyoximato(2-)-(triphenylphosphine)rhodate] complex: a vinylene-bridged dinuclear rhodium complex

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Abstract

$[Rh(dmgH)_2(PPh_3)]^-$ ($dmgH_2$ = dimethylglyoxime), prepared by reduction of $[Rh(dmgH)_2(PPh_3)Cl]$ with $NaBH_4$ in methanolic KOH, reacts with (*E*)-1,2-dichloro ethylene to give the (*E*)-vinylene-bridged dinuclear rhodium complex $[\{K(MeOH)_2\}_2\{(PPh_3)(dmg)(dmgH)Rh-CH=CH-Rh(dmg)(dmgH)(PPh_3)\}]$ (**1**). Furthermore, **1** is formed in a mixture with $[Rh(dmgH)_2(PPh_3)(Z)-CH=CHCl]$ (**2**) and $[Rh(dmgH)_2(PPh_3)CH=CH_2]$ (**3**) in the reaction of $[Rh(dmgH)_2(PPh_3)]^-$ with (*Z*)-ClCH=CHCl and in a mixture with **3** in the reaction of $[Rh(dmgH)_2(PPh_3)]^-$ with acetylene.

1 crystallizes in the monoclinic space group *C*2/*c* with: $a = 22.711(5)$, $b = 10.465(2)$, $c = 27.910(6)$ Å, $\beta = 101.71(3)°$, $Z = 4$. The structure was refined up to $R1 = 0.0373$ for 4903 reflections. The molecule consists of two [Rh(dmg)(dmgH)(PPh$_3$)] subunits linked by an (*E*)-CH=CH bridge. The oxygen atoms of the dimethylglyoximato ligands and the solvent molecules (MeOH) are coordinated at the potassium ions.

^1H, ^{13}C and ^{31}P NMR spectra of **1** agree definitely with the molecular structure in solid state, as was shown by comparison of the experimental spectra with the computer simulated spectra on the basis of AA'MM'XX', AMM'XX' and AA'XX' spin systems for the vinylene protons, the carbon atoms and the phosphorus atoms respectively. In $CDCl_3/CD_3COOD$ the neutral complex $[(PPh_3)(dmgH)_2Rh-CH=CH-Rh(dmgH)_2(PPh_3)]$ (**1'**) is formed, as was shown by ^1H, ^{13}C and ^{31}P NMR spectroscopy.

Keywords: Rhodium complexes; Organorhodoximes; Bimetallic complexes; Vinylene-bridged complexes; Crystal structures

1. Introduction

With regard to our investigations on alkyne complexes and metal-catalyzed functionalization reactions of acetylene [1], we were interested in dinuclear transition metal complexes having a $(CH)_2$ bridge. Apart from the well-known complexes **A** with a μ-⊥- or di-π-coordinated acetylene, complexes **B** and **C** with di-σ bonded vinylene-bridges and complexes **D** with bridging bis(carben) ligands are known [2–5]. In the (*cis-/Z-*) complexes **B** the metal centers are often linked by a metal–metal bond (dimetallacyclobutene complexes) and/or by other bridging ligands [3,4]. (*trans-/E-*) Complexes **C** can be stabilized by an agostic metal–CH interaction [6,7].

There are only a few examples of transition metal complexes (*trans-/E*)-M–CH=CH–M' (**C**) (M/M' = Co/Co [8], Rh/Rh [9], Ru/Zr [7]) and only one of them, $[Cp(PMe_3)_2Ru-CH=CH-ZrClCp_2]$, is structurally characterized [7]. These complexes can be regarded as prototypes for analogous complexes with bridges –CR=CR–, where R represents substituents, especially electron-withdrawing ones [3,4,10]. Here we report the synthesis and molecular structure of a vinylene-bridged dinuclear rhodium complex.

2. Results and discussion

2.1. Synthesis

$[Rh(dmgH)_2(PPh_3)]^-$, prepared by reduction of $[Rh(dmgH)_2(PPh_3)Cl]$ with $NaBH_4$ in methanolic KOH

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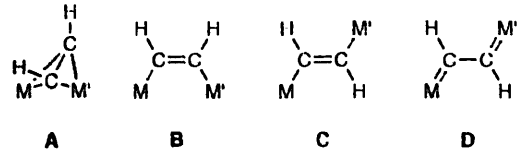
[11,12], reacts with (*E*)-1,2-dichloro ethylene to give a μ-(*E*)-vinylene-bis[dimethylglyoximato(1-)-dimethylglyoximato(2-)-(triphenylphosphine)rhodate] complex **1** (see Eq. (1)).



(1)

$$[Rh(dmgH)_2(PPh_3)Cl] \xrightarrow[MeOH/KOH]{NaBH_4} [Rh(dmgH)_2(PPh)_3]^- \xrightarrow{(E)\text{-}ClCH=CHCl}$$

$$[\{K(MeOH)_2\}_2\{(PPh_3)(dmg)(dmgH)Rh\text{-}CH=CH\text{-}Rh(dmg)(dmgH)(PPh_3)\}]$$

1

Complex **1** precipitates as a yellow colored crystalline substance (yield: 56–75%). It is insoluble in all common solvents but sparingly soluble in a mixture of chloroform and methanol. BrCH=CHBr, used as an (*E,Z*)-mixture (40/60), reacts in the same way but with a lower yield of about 25%.

(*Z*)-1,2-dichloro ethylene reacts with $[Rh(dmgH)_2(PPh_3)]^-$ much more slowly than the (*E*)-isomer to give complex **1** in a mixture with the (*Z*)-2-chlorovinyl complex $[Rh(dmgH)_2(PPh_3)(Z)\text{-}CH=CHCl]$ (**2**) and the vinyl complex $[Rh(dmgH)_2(PPh_3)CH=CH_2]$ (**3**) (**1**/**2**/**3** = 20/30/50). It might be that the formation of **1** proceeds via **2** as an intermediate followed by a dehydrohalogenation reaction in the strong alkaline media to give an acetylide complex at which $[Rh(dmgH)_2(PPh_3)]^-$ is nucleophilic added. Otherwise (*Z*)-ClCH=CHCl could be a subject of dehydrohalogenation to give HC≡CCl as an intermediate which reacts in the sense of an oxidative and a nucleophilic addition with $[Rh(dmgH)_2(PPh_3)]^-$ to give **1**. The formation of the vinyl complex **3** is in accordance with our earlier investigations [12,13] in which we shown that BrC≡CPh and BrC≡CPr react with $[Rh(dmgH)_2(PPh_3)]^-$ to give vinyl complexes $[Rh(dmgH)_2(PPh_3)R]$ (R = CH=CHPh, CH=CHPr) as the main products.

Perchloroethylene reacts also with $[Rh(dmgH)_2(PPh_3)]^-$ to give the dinuclear complex **1**, the (*Z*)-2-chlorovinyl complex **2**, the vinyl complex **3** and $[Rh(dmgH)_2(PPh_3)Cl]$ in a ratio 15/20/5/60. Acetylene reacts with $[Rh(dmgH)_2(PPh_3)]^-$ to give the vinyl complex **3** as the main product (greater than 80%) and the dinuclear complex **1** as side product (ca. 10%).

Complex **1** can be isolated as methanol adduct in well shaped crystals at slow combining of $[Rh(dmgH)_2(PPh_3)]^-$ with (*E*)-ClCH=CHCl without stirring. Apart from weathering within a few minutes,

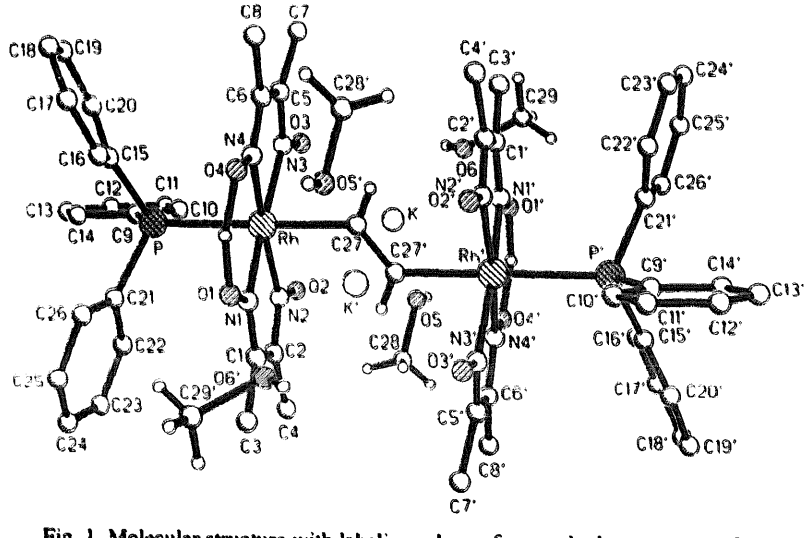


Fig. 1. Molecular structure with labeling scheme for non-hydrogen atoms of **1**.

the crystals are air-stable. In $CHCl_3$/HOAc (1/1 v/v) a protolysis reaction takes place within 30 min to give the vinyl complex **3** and [Rh(dmgH)$_2$(PPh_3)OAc].

2.2. Molecular and crystal structure

The molecular structure of **1**, including the numbering scheme, is shown in Fig. 1. Selected bond lengths and angles are listed in Table 1. The C_i point group symmetry is realized by the complex within the crystal. The Rh atoms in **1** exhibit a distorted octahedral coordination; the two dimethylglyoximato ligands lie in the equatorial plane and the triphenylphosphine and the bridging vinylene groups occupy the axial positions. The two dimethylglyoximato ligands of the [Rh(dmgH)(dmg)] units are tilted away from the PPh_3 ligands ($\alpha = 7.1(1)°$, where α is the angle between the normal vectors of the least squares planes of dmgH and dmg ligands, see Ref. [14]) resulting in a displacement of the Rh atom from the mean plane through the four oxime N donor atoms at 0.0909(8) Å in the direction of the P atom.

In contrast to the observations made for a series of closely related mononuclear organorhodoximes [Rh(dmgH)$_2$(PPh_3)R] [15–20], where the two dimethylglyoximato ligands are stabilized by two intramolecular hydrogen bonds, only one approximately symmetrically arranged hydrogen bond is observed in **1**: O4–H4 1.30(8) Å, O1–H4 1.20(8) Å, O1 · · · O4 2.464(4) Å and O1–H4–O4 160(5)°. Compared with that, the distance between the oxygen atoms O2 · · · O3, which are not bridged by a hydrogen bond, is much longer and amounts to 3.276(4) Å.

The P–Rh–C unit is nearly linear (P–Rh–C27 178.9(1)°). In comparison with the analogous vinyl

Table 1
Selected bond lengths (Å) and angles (deg) for **1**

Rh–P	2.427(1)	P–Rh–C27	178.9(1)
Rh–N1	1.985(3)	P–Rh–N1	90.6(1)
Rh–N2	2.042(3)	P–Rh–N2	92.0(1)
Rh–N3	2.057(3)	P–Rh–N3	94.4(1)
Rh–N4	1.995(3)	P–Rh–N4	93.2(1)
Rh–C27	2.072(3)	N1–Rh–N2	78.3(1)
P–C9	1.827(4)	N1–Rh–N3	172.3(1)
P–C15	1.832(3)	N1–Rh–N4	96.2(1)
P–C21	1.837(3)	N1–Rh–C27	89.8(1)
O1–N1	1.355(4)	N2–Rh–N3	107.4(1)
O2–N2	1.310(4)	N2–Rh–N4	172.5(1)
O3–N3	1.303(4)	N2–Rh–C27	89.1(1)
O4–N4	1.360(4)	N3–Rh–N4	77.7(1)
N1–C1	1.287(5)	N3–Rh–C27	85.2(1)
N2–C2	1.304(5)	N4–Rh–C27	85.7(1)
N3–C5	1.313(4)	Rh–P–C9	120.1(1)
N4–C6	1.284(5)	Rh–P–C15	111.6(1)
C27–C27′	1.287(6)	Rh–P–C21	111.5(1)
		C9–P–C15	103.7(2)
C1–C2 [a]	1.1(1)	C9–P–C21	100.7(2)
C5–C6 [b]	4.0(1)	C15–P–C21	108.2(2)

[a] Twist angle around the C1–C2 bond for the ligand N1,N2,O1,O2,C1–C4.
[b] Twist angle around the C5–C6 bond for the ligand N3,N4,O3,O4,C5–C8.

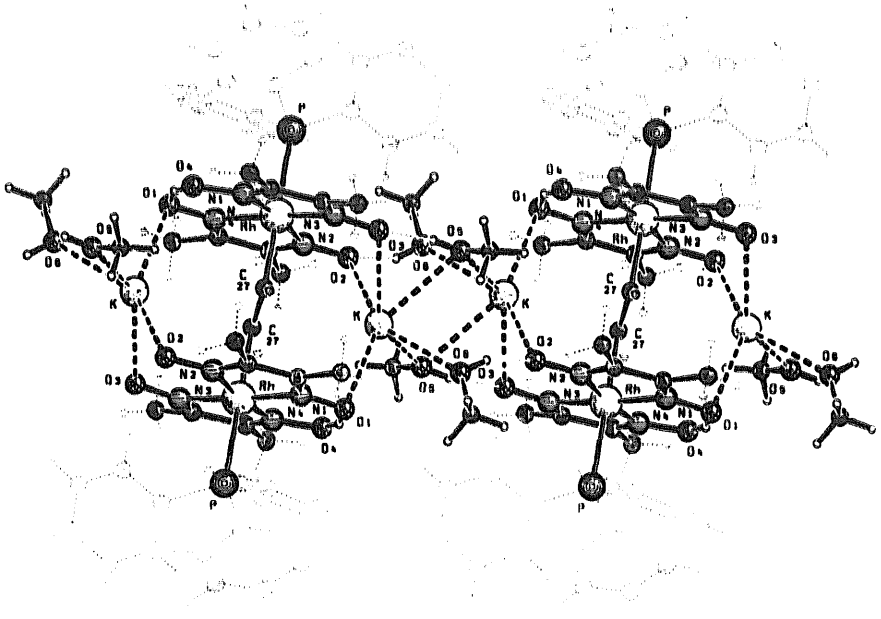


Fig. 2. Packing diagram of **1** showing all potassium contacts less than 3.0 Å (distances (Å), angles (deg)): K–O2 2.759(3), K–O3 2.755(3), K–O6 2.946(6), K–O1$^{\#1}$ 2.800(3), K–O5$^{\#2}$ 2.718(5), K–O5$^{\#3}$ 2.968(5). Intermolecular hydrogen bonds: O5–H5 · · · O3$^{\#4}$ (O5 · · · O3 2.641(5), O5–H5 0.82(3), H5 · · · O3 1.88(3), ∠O5–H5–O3 154(4)), O6–H6 · · · O2$^{\#5}$ (O6 · · · O2 2.682(6), O6–H6 0.82(4), H6 · · · O2 1.99(4), ∠O6–H6–O2 142(5)). Symmetry: #1 0.5 − x, 0.5 − y, 1 − z; #2: x, −y, 0.5 + z; #3: 0.5 − x, 0.5 − y, 0.5 − z; #4: 0.5 − x, 0.5 + y, 0.5 − z. #5: 0.5 − x, −0.5 − y, 1 − z.

complex $[Rh(dmgH)_2(PPh_3)CH{=}CH_2]$ (2) [18], the Rh–C bond in 1 is significantly longer (2.072(3) vs. 2.035(3) Å) and the Rh–P bond is significantly shorter (2.427(1) vs. 2.447(1) Å). Neglecting an influence which might arise from the twofold deprotonated dimethylglyoxime moiety, the vinylene ligand can be arranged in the following (structural) trans-influence series derived from the Rh–P bond lengths in organorhodoximes $[Rh(dmgH)_2(PPh_3)R]$ and $[Rh(dmgH)_2(PPh_3)Cl]$ (R (d(Rh–P) Å)): ^{t}Bu (2.492(1) [15]) ~ ^{i}Pr (2.489(2) [16]) > Et (2.461(2) [17]) ~ Me (2.455(1) [19]) > $CH{=}CH_2$ (2.447(1) [18]) > (*E*)-CH=CH– (2.427(1)) > C≡CPh (2.409(1) [20]) ≫ Cl (2.327(1) [21]).

Both the oxygen atoms of the dimethylglyoximato ligands and of the two solvent molecules (methanol) are coordinated at the potassium ion (Fig. 2). One of the methanol molecules (O5, C28) is bridging two potassium cations via hydrogen bonds. Additionally, the molecules are linked together by intermolecular hydrogen bonds under inclusion of solvent molecules. All these contacts are leading to the formation of two-dimensionally extended ribbons along [010].

2.3. NMR spectroscopy

The results of ^{1}H, ^{13}C and ^{31}P NMR spectroscopic measurements of 1 in $CDCl_3/CD_3OD$ (500–1000/1 v/v) are summarized in Table 2. Furthermore, the values are given for the protonated complex $[(PPh_3)(dmgH)_2Rh{-}CH{=}CH{-}Rh(dmgH)_2(PPh_3)]$ (1′) which was obtained by addition of CD_3COOD to a suspension of 1 in $CDCl_3$ ($CDCl_3/CD_3COOD$ = 30/1 v/v). Without Rh–C bond splitting, 1′ is stable in this solvent mixture for 2 h at least.

In accordance with the structure of complex 1, the azomethine C atoms, as well as the C and H atoms of the methyl groups of the dmgH and dmg ligands, are not chemically equivalent. However, they are equivalent in complex 1′.

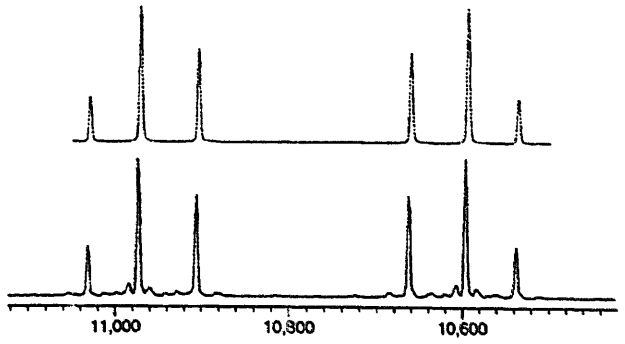


Fig. 3. Experimental (below; with minor signals from ^{13}C satellite spectra) and simulated (above) 202 MHz ^{31}P-{^{1}H} NMR spectrum of 1.

The ^{31}P-{^{1}H} spectrum is the AA′ part of an AA′XX′ spin system (A = ^{31}P, X = ^{103}Rh). Computer simulation gave the couplings (the values for 1″ are given in parentheses): $^1J(^{103}Rh,^{31}P)$ = 73.2 Hz (65.9 Hz), $^3J(^{31}P,^{31}P)$ = 25.5 Hz (32.1 Hz), $^4J(^{103}Rh,^{31}P)$ = 3.1 Hz (3.6 Hz) ($^3J(^{103}Rh,^{103}Rh)$ ca. 0 Hz); see Fig. 3.

The assignment of the ^{13}C signals was checked by an attached proton test (APT) spectrum. Thus, the multiplet of the *ipso*-C atom could be clearly separated from those of the other phenyl carbon atoms. The multiplets are the A part of the AMM′XX′ spin systems (A = ^{13}C, M = ^{31}P, X = ^{103}Rh), or of the AMNXY spin systems when the isotopomers (^{13}C ~ P–Rh–CH=CH–Rh–P ~ ^{12}C) are taken into account. Computer simulation gave the couplings $^2J(^{31}P,^{13}C_\alpha)$ = 11.1 Hz (10.4 Hz) and $^3J(^{31}P,^{13}C_m)$ = 9.2 Hz (8.8 Hz). These values are very similar to those in mononuclear organorhodoximes $[Rh(dmgH)_2(PPh_3)R]$ [12,22,23]. Owing to the lower intensity of the *ipso*- and vinylene-C signals, the couplings cannot be proved beyond doubt. The calculated

Table 2
NMR spectral data for complexes 1 and 1′

	1 in $CDCl_3/CD_3OD$			1′ in $CDCl_3/CD_3COOD$		
	$\delta(^1H)$ (ppm)	$\delta(^{13}C)$ (ppm)	$\delta(^{31}P)$ (ppm)	$\delta(^1H)$ (ppm)	$\delta(^{13}C)$ (ppm)	$\delta(^{31}P)$ (ppm)
dmgH / dmg						
CH_3	1.57 (d [a]), 1.62 (d [b])	11.5, 11.6		1.77 (d [c])	11.7	
C=N		146.0, 150.0			149.3	
PPh_3	7.2–7.4 (m)		10.8 (m)	7.2–7.4 (m)		8.02 (m)
C_i		130.5 (m)			130.1 (m)	
C_o		133.6 [d]			133.3 [d]	
C_m		127.4 [d]			129.0 [d]	
C_p		129.2 (s)			129.7 (s)	
–CH=CH–	4.44 [e]	139.2 (m)		4.84 [e]	134.0 (m)	
MeOH	3.40 (s)	49.4 (s)		3.37 (s)	50.2 (s)	

[a] $^5J(^{31}P,^1H)$ = 0.78 Hz; [b] $^5J(^{31}P,^1H)$ = 1.76 Hz; [c] $^5J(^{31}P,^1H)$ = 1.91 Hz; [d] filled in doublet; [e] triple of triplets with additional splitting of the two middle lines (less than 1 Hz) of the outer triplets.

values for **1** ($^1J(^{31}P,^{13}C_i) = 32$ Hz, $^2J(^{31}P,^{13}C_{=CH}) = 91$ Hz, $^1J(^{103}Rh,^{13}C_{=CH}) = 24$ Hz) are similar to those in the mononuclear vinyl complex **3** ($^1J(^{31}P,^{13}C_i) = 30.3$ Hz, $^2J(^{31}P,^{13}C_{=CH}) = 96.3$ Hz, $^1J(^{103}Rh,^{13}C_{=CH}) = 26.2$ Hz) [12,22].

The vinylene proton signals in **1** and **1'** exhibit the same spectral pattern apart from a shift difference of about 0.4 ppm (Table 2). There are relatively broad lines (even at 500 MHz) pointing to a dynamic process. The pattern can be regarded as an AA' part of an AA'MM'XX' spin system. Using the P,P and Rh,P couplings from the ^{31}P spectrum, the simulation gave $^2J(^{103}Rh,^1H)$, $^3J(^{103}Rh,^1H) \leq 1$ Hz, $^3J(^{31}P,^1H) \approx 5$ Hz and $^4J(^{31}P,^1H) \approx 8$ Hz. The spectral pattern is relatively insensitive to variation of $^3J(^1H,^1H)$. The 'information' on this coupling is only in the splitting of the two middle lines of the two outer triplets. When the coupling $^3J(^1H,^1H)$ is varied between 10 and 30 Hz, the agreement between experimental and calculated spectra is good. This is a further proof for the trans structure of **1**.

Complex **1** is the only example of a spectroscopically and structurally characterized dinuclear organometallic complex in which two electron-rich metals are linked by an (*E*)-CH=CH unit. $[Cp(PMe_3)_2Ru-CH=CH-ZrClCp_2]$ with its electron-rich and electron-deficient metal is characterized by a β-agostic interaction between the Zr center and CH adjacent to Ru [7].

3. Experimental

All manipulations were performed under an atmosphere of purified argon with use of standard Schlenk techniques, and all solvents were distilled from appropriate drying agents. Elemental analyses were carried out at the Microanalytical Lab. of the Chemical Department. Infrared spectra were measured on a Specord 75 IR (KBr). ^1H, ^{13}C and ^{31}P NMR spectra were recorded at ambient temperature on Gemini 200 (Varian) or Unity 500 (Varian) spectrometers. Solvent signals (^1H, ^{13}C) and 85% H_3PO_4 (^{31}P) were used as internal and external standards. The coupling constants were simulated with the program PERCH [24]. $[Rh(dmgH)_2(PPh_3)Cl]$ was prepared according to the literature [25]. The organo halides were commercially available.

3.1. $[\{K(MeOH)_2\}_2\{(PPh_3)(dmg)(dmgH)Rh-CH=CH-Rh(dmg)(dmgH)(PPh_3)\}]$ (1)

To a solution of $[Rh(dmgH)_2(PPh_3)Cl]$ (946 mg, 1.5 mmol) in methanolic KOH (75 ml, 0.15 M), a solution of $NaBH_4$ (76 mg, 2.0 mmol) in methanolic KOH (25 ml, 0.15 M) is added dropwise and stirred for 2 h at 20 °C to give a deep violet solution of $[Rh(dmgH)_2(PPh_3)]^-$. To this, a solution of (*E*)-ClCH=CHCl (291 mg, 3.0 mmol) in methanol (25 ml)

Table 3
Crystal data and details of data collection and refinement for **1**

Formula	$C_{58}H_{74}K_2N_8O_{12}P_2Rh_2$
Color/shape	yellow block, 0.8 × 0.59 × 0.46 mm^3
Formula weight (g mol^{-1})	1421.23
Space group	C2/c (No. 15)
Cell constants	
a (Å)	22.711(5)
b (Å)	10.465(2)
c (Å)	27.910(6)
β (deg)	101.71(3)
Cell volume (Å^3)	6495(3)
Formula units/unit cell	4
D_{calc} (g cm^{-3})	1.453
Scan method	ω–2θ
Scan width	1.05–1.20, variable
Standard reflections	600, 00 – 16, 0 – 46
Decay of standards	±5.2%
2θ range (deg)	$3.0 \leq 2\theta \leq 50.0$
Range of *h*,*k*,*l*	±26, 0/12, 0/33 and ±26, – 12/0, – 33/0
Reflections measured	12259
Reflections unique	5735
Refl. Observed ($I_o \geq 2.0\sigma(I_o)$)	5486 (only applied for negative intensities)
No. of parameters varied	397
Weights	$1/\sigma^2(F_o^2)^2 + (0.0372P)^2 + 9.69P$, $P = (F_o^2 + 2F_c^2)/3$
GOF (F^2)	1.210
*wR*2 (F^2)	0.0991
*R*1 (F)	0.0373 (for 4903 reflections with $F_o \geq 4.0\sigma(F_o)$)
Min./max. residual electron density (e Å^{-3})	–0.55/0.85

is added within 15 min and stirred for 30 min. The precipitated complex **1** is filtered and dried in vacuo. Yield 500–800 mg (56–75%).

$C_{58}H_{74}K_2N_8O_{12}P_2Rh_2$ (1421.23): anal. (exp./calc.) C, 47.61/49.02; H, 4.81/5.25; N, 7.88/7.88%. IR (KBr, cm^{-1}): 485 w, 515 vs, 695 vs, 740 s, 980 w, 990 w, 1020 w, 1080 s, 1110 w, 1250 vs, 1380 w, 1420 vs, 1480 w, 1550 m, 2900 w, 3030 m.

3.2. *[Rh(dmgH)$_2$(PPh$_3$)(Z)-CH=CHCl] (2) and [Rh(dmgH)$_2$(PPh$_3$)CH=CH$_2$] (3)*

As described above, to a solution of $[Rh(dmgH)_2(PPh_3)]^-$ (1.5 mmol) in methanolic KOH (100 ml, 0.15 M) (*Z*)-ClCH=CHCl (291 mg, 3.0 mmol) was added. After stirring for 96 h (**1**/**2**/**3** = 20/30/50) the solution was treated with CO_2/H_2O (pH 7–8), extracted with methylene chloride and chromatographed on silica gel 60 (Merck) affording a mixture of **2** and **3** (35/65; 50 mg).

2: ^{1}H NMR ($CDCl_3$): δ(Me) = 1.83 (^5J(P,H) = 2.0 Hz), δ(CH=) = 5.95 (^3J(H,H) = 6.5 Hz, ^2J(Rh,H) = 2.0 Hz, ^3J(P,H) = 2.0 Hz), δ(=CHCl) = 6.26 ppm (^3J(Rh,H) = 2.3 Hz, ^4J(P,H) = 19.1 Hz). ^{13}C NMR ($CDCl_3$): δ(C=N) = 149.7, δ(CH_3) = 11.4, δ(C_i) = 129.1 (^1J(P,C) = 34.4 Hz), δ(C_o) = 133.5 (^2J(P,C) = 10.4 Hz), δ(C_m) = 128.1 (^3J(P,C) = 9.5 Hz), δ(C_p) = 130.1 (^4J(P,C) = 2.3 Hz), δ(CH=) = 139.4 (^1J(Rh,C) = 30.9 Hz, ^2J(P,C) = 107.1 Hz), δ(=CHCl) = 123.0 ppm (^2J(Rh,C) = 1.6 Hz, ^3J(P,C) = 3.2 Hz). ^{31}P NMR ($CDCl_3$): δ = 9.26 ppm (^1J(Rh,P) = 67.5 Hz).

3: ^{1}H NMR ($CDCl_3$): δ(Me) = 1.84 (^5J(P,H) = 1.9 Hz), δ(CH=) = 6.27 ($^3J(H,H_{cis})$ = 8.2 Hz, $^3J(H,H_{trans})$ = 16.4 Hz, ^2J(Rh,H) = 1.3 Hz, ^3J(P,H) = 8.2 Hz), δ(=CH_{cis}H) = 5.10 (^3J(Rh,H) = 2.3 Hz, ^4J(P,H) = 22.2 Hz), δ(=CH_{trans}H) = 4.78 ppm (^3J(Rh,H) = 1.4 Hz, ^4J(P,H) = 9.8 Hz). ^{13}C NMR ($CDCl_3$): δ(C=N) = 148.8, δ(CH_3) = 11.6, δ(C_i) = 130.0 (^1J(P,C) = 30.3 Hz), δ(C_o) = 133.4 (^2J(P,C) = 10.8 Hz), δ(C_m) = 128.1 (^3J(P,C) = 8.9 Hz), δ(C_p) = 129.9 (^4J(P,C) = 2.1 Hz), δ(CH=) = 152.2 (^1J(Rh,C) = 26.2 Hz, ^2J(P,C) = 96.3 Hz), δ(=CH_2) = 117.9 ppm. ^{31}P NMR ($CDCl_3$): δ = 8.61 ppm (^1J(Rh,P) = 62.7 Hz).

The spectra are identical with authentic samples prepared by reaction of $[Rh(dmgH)_2(PPh_3)]^-$ with ClCH=CCl_2 [22] and CH_2=CHCl respectively [12].

3.3. *Crystallographic studies*

Crystal data and details of the data collection and refinement for **1** are summarized in Table 3. As the crystals rapidly undergo weathering when removed from the mother liquor, a single crystal of 0.8 × 0.59 × 0.46 mm^3 size was mounted in a glass capillary which was filled with the solvent. All X-ray data were collected at room temperature on a Stoe STADI 4 four-circle diffractometer using Mo Kα radiation (λ = 0.71073 Å, graphite-monochromator). Lattice parameters were derived from a least squares treatment of the 2θ-angles of 92 reflections ($20.0 \le 2\theta < 26.0°$). The structure was solved by direct methods using the program SHELXS-86 [26]. The structure refinement was carried out by full-matrix least squares procedures on F^2 (SHELXL-93 [27]). The hydrogen atoms of the phenyl rings and of the methyl groups are located in geometrically calculated positions with *U* values calculated as being 1.2 times the U_{iso}-value of the corresponding C-atoms. The vinylene hydrogen H27 and the bridging hydrogen H4 of the dimethylglyoximato-ligands have been located in a difference Fourier and isotropically refined. Figures were drawn with SCHAKAL program [28]. Further details of the crystal structure analysis can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, citing the deposition no. CSD-404666.

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