

An unusual selective reduction of an oxime into an imine group in halogenomethyl rhodoximes

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Abstract

$[\text{Rh}(\text{dmgH})_2(\text{PPh}_3)]^-$ ($[\text{Rh}]^-$, **1**) $\{[\text{Rh}] = [\text{Rh}(\text{dmgH})_2(\text{PPh}_3)]\}$; ($\text{dmgH})_2$ = dimethylglyoxime, obtained by reduction of $[\text{Rh}]-\text{Cl}$ with NaBH_4 in methanolic KOH, reacts with dihalogenomethanes CH_2X_2 ($\text{X} = \text{Br}, \text{Cl}$) to give besides the known complexes $[\text{Rh}]-\text{CH}_2\text{X}$ ($\text{X} = \text{Br}$, **2a**; $\text{X} = \text{Cl}$, **2b**) the complexes $[\text{Rh}(\text{CH}_2\text{X})\{\text{ON}=\text{C}(\text{Me})-\text{C}(\text{Me})=\text{NH}\}(\text{dmgH})(\text{PPh}_3)]$ ($\text{X} = \text{Br}$, **3a**; $\text{X} = \text{Cl}$, **3b**) where one oxime unit is reduced to an imine. Due to the strong alkaline medium (methanolic KOH) **3a** was found to react partially, yielding $[\text{Rh}(\text{CH}_2\text{OMe})\{\text{ON}=\text{C}(\text{Me})-\text{C}(\text{Me})=\text{NH}\}(\text{dmgH})(\text{PPh}_3)]$ (**3c**). All three complexes were characterized by ^1H -, ^{13}C -, ^{31}P -NMR spectroscopy. **3a** crystallizes in the triclinic space group $P\bar{1}$ with two molecules in the asymmetric unit. These molecules are linked via two $\text{N}-\text{H}\cdots\text{O}$ hydrogen bridges forming a dimer. The rhodium atoms display a distorted octahedral coordination with the $\text{dmgH}/\text{ON}=\text{C}(\text{Me})-\text{C}(\text{Me})=\text{NH}$ ligands in the equatorial plane and PPh_3 and the CH_2Br ligands in the axial positions. © 1998 Elsevier Science S.A. All rights reserved.

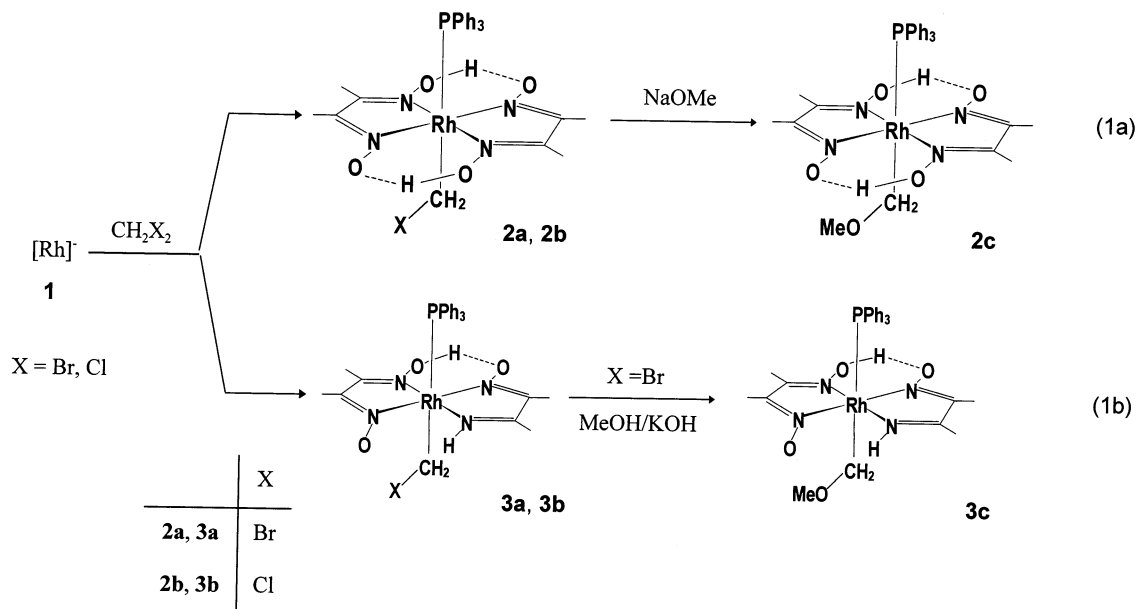
Keywords: Rhodium complexes; Organorhodoximes; Oxime–imine moiety; Crystal structure

1. Introduction

Since the first preparation of organorhodoximes $[\text{Rh}(\text{dmgH})_2(\text{L})\text{R}]$ ($\text{L} = \text{py}$; $\text{R} = \text{Me}, \text{Et}, \text{CH}_2\text{CH}_2\text{CN}$) by Weber and Schrauzer [1] in 1970, there have been synthesized numerous organorhodoximes with various axial bases ($\text{L} = \text{PPh}_3, \text{PMe}_3, \text{H}_2\text{O}, \text{py}, \dots$) and a wide variety of organo ligands ($\text{R} = \text{alkyl}, \text{aryl}, \text{vinyl}, \text{alkynyl}, \text{allenyl}, \text{functionalized organo ligands}$) [2,3]. Recently, dinuclear oligo–methylene bridged complexes $[\text{Rh}](\text{CH}_2)_n[\text{Rh}]$ ($n = 2-5$) and a vinylene bridged complex, $[\{\text{K}(\text{MeOH})_2\}_2\{(\text{PPh}_3)(\text{dmg})(\text{dmgH})\text{Rh}-\text{CH}=\text{CH}-\text{Rh}(\text{dmg})(\text{dmgH})(\text{PPh}_3)\}]$, were also prepared and characterized by NMR spectroscopy and by X-ray structure analysis [4,5]. Especially the triphenylphosphine complexes $[\text{Rh}]-\text{R}$ were used to study the structural and the NMR *trans* influence of R with the bond length $d(\text{Rh}-\text{P})$ and the coupling constant $^1J(^{103}\text{Rh}, ^{13}\text{C})$, respectively, as measure [3].

In all these reactions the pseudomacrocyclic ligand system $(\text{dmgH})_2$ proved to be very stable apart from protonation/deprotonation equilibria involving the hydrogen bonds [6] and modifications replacing the hydrogen bridges with boron bridges [7]. Only very recently, there has been observed axial–equatorial ligand ($\text{R}/(\text{dmgH})_2$) interactions: Thus, the OH group of the (*Z*)-3-hydroxy-3-methyl-but-1-enyl ligand in $[\text{Rh}]-\text{CH}=\text{CH}-\text{CMe}_2\text{OH}$ act as both hydrogen donor and acceptor forming two strong hydrogen bonds to the equatorial $(\text{dmgH})_2$ ligand with cleavage an $\text{O}-\text{H}-\text{O}$ bond between them [8]. Furthermore, $[\text{Rh}]^-$ was found to react with $\text{X}(\text{CH}_2)_n\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, n = 3-5$) via $[\text{Rh}](\text{CH}_2)_n\text{X}$ as intermediates, yielding cyclic organorhodoximes $[\text{Rh}\{(\text{CH}_2)_n-\text{ON}=\text{C}(\text{Me})-\text{C}(\text{Me})=\text{NO}\}(\text{dmgH})(\text{PPh}_3)]$ [4]. Their formation can be understood as an interligand nucleophilic substitution reaction of an equatorial oximato group with the $\text{C}-\text{X}$ group of the ligated axial ω -halogenoalkyl ligand in the intermediate $[\text{Rh}](\text{CH}_2)_n\text{X}$. Recently, a reduction of

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Scheme 1.

an oxime to an imine group was observed upon the reaction of $[\text{Rh}(\text{dmgH})(\text{dmgH}_2)\text{Cl}_2]/\text{NaBH}_4$ with phosphines [9].

Bromo- and chloromethyl rhodoximes $[\text{Rh}]-\text{CH}_2\text{X}$ ($\text{X} = \text{Br}, \text{Cl}$) are rather reactive. They react with NaOMe in a nucleophilic substitution reaction to give the methoxymethyl complex ($\text{X} = \text{OMe}$) ([3]a). An analogous reaction was found in the cobaloximes [10]. But three-membered $\text{Co}-\text{N}-\text{C}$ rings were formed by using closely related equatorial imine/oxime ligands instead of the bis(dimethylglyoximate) ligands [11].

Here we report the reaction of $[\text{Rh}]^-$ with CH_2Br_2 and CH_2Cl_2 in methanolic KOH to give not only the expected complexes $[\text{Rh}]-\text{CH}_2\text{X}$ ($\text{X} = \text{Br}, \text{Cl}, \text{OMe}$) but also unprecedented reduction reactions to give $[\text{Rh}(\text{CH}_2\text{X})\{\text{ON}=\text{C}(\text{Me})-\text{C}(\text{Me})=\text{NH}\}(\text{dmgH})(\text{PPh}_3)]$ where one oxime unit is reduced to an imine moiety.

2. Results and discussion

2.1. Synthesis

$[\text{Rh}]^-$ (**1**), prepared by reduction of $[\text{Rh}]-\text{Cl}$ with NaBH_4 in methanolic KOH [12], reacts with CH_2Br_2 and CH_2Cl_2 to give the known bromo- and chloromethyl complexes $[\text{Rh}]-\text{CH}_2\text{X}$ ($\text{X} = \text{Br}$ **2a**, yield: 14%; $\text{X} = \text{Cl}$ **2b**, yield: 74%). These complexes react with NaOMe to produce the methoxymethyl complex $[\text{Rh}]-\text{CH}_2\text{OMe}$ **2c** (yield: 37–47%) ([3]a) (see Scheme 1a).

Besides the formation of **2**, CH_2X_2 ($\text{X} = \text{Br}, \text{Cl}$) reacts with $[\text{Rh}]^-$ to give the complexes $[\text{Rh}(\text{CH}_2\text{X})\{\text{ON}=\text{C}(\text{Me})-\text{C}(\text{Me})=\text{NH}\}(\text{dmgH})(\text{PPh}_3)]$ ($\text{X} = \text{Br}$, **3a**;

$\text{X} = \text{Cl}$, **3b**) (Scheme 1b) where one oxime unit of the equatorial ligand $(\text{dmgH})_2$ is reduced into an imine group.

The yield of the reduced chloromethyl complex **3b** is only ca. 5%, whereas the chloromethyl complex with the unchanged $(\text{dmgH})_2$ ligand **2b** is formed in about 40% yield. Fast mixing of CH_2Br_2 and $[\text{Rh}]^-$ affords the reduced bromomethyl complex **3a** in about 50% yield. By adding CH_2Br_2 to $[\text{Rh}]^-$ over a period of 3 h, a substitution reaction takes also place to give the reduced methoxymethyl complex $[\text{Rh}(\text{CH}_2\text{OMe})\{\text{ON}=\text{C}(\text{Me})-\text{C}(\text{Me})=\text{NH}\}(\text{dmgH})(\text{PPh}_3)]$ (**3c**) due to the strong alkaline medium (methanolic KOH). The total yield of the two reduced complexes is about 20% (**3a**:**3c** ca. 1:1). The isolated reduced bromomethyl complex **3a** undergoes in methanolic KOH (20 h, r.t.) the same substitution reaction to form the methoxymethyl complex **3c**, with a yield of about 20%.

The reduced bromomethyl complex **3a** was isolated as yellow crystals. Because of the low yield and the similar solubility in common organic solvents, the reduced chloromethyl complex **3b** was obtained after recrystallization from acetone/heptane (four times) only in a mixture with the non-reduced chloromethyl complex **2b** (**3b**:**2b** ca. 4:1). For the same reason the methoxymethyl complex **3c** was obtained in a mixture with complex **3a** (ca. 1:1). All complexes were fully characterized by NMR spectroscopy (^1H , ^{13}C , ^{31}P) and complex **3a** by X-ray structure analysis, too. Complex **3a** is monomer in CHCl_3 as was shown by osmometric molecular weight determination (found 669.8 g mol^{-1} , calc. for $[\text{Rh}(\text{CH}_2\text{Br})\{\text{ON}=\text{C}(\text{Me})-\text{C}(\text{Me})=\text{NH}\}(\text{dmgH})(\text{PPh}_3)]$ 673.3 g mol^{-1}).

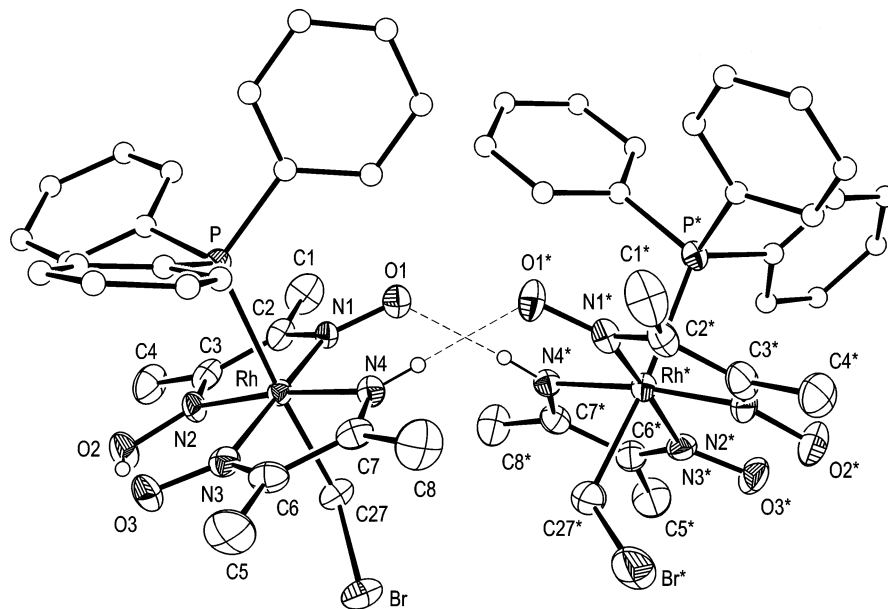


Fig. 1. Molecular structure of $[\text{Rh}(\text{CH}_2\text{Br})\{\text{ON}=\text{C}(\text{Me})-\text{C}(\text{Me})=\text{NH}\}(\text{dmgH})(\text{PPh}_3)]$ **3a**.

2.2. Structure

The molecular structure of **3a** is shown in Fig. 1. Selected bond lengths and angles are listed in Table 1. **3a** crystallizes in the triclinic space group $P\bar{1}$ with two molecules in the asymmetric unit. These molecules are linked via two $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds forming a dimer. The $\text{N}\cdots\text{O}$ distances ($\text{N}4\cdots\text{O}1$ 2.873(6),

$\text{N}4\cdots\text{O}1^*$ 2.908(6) Å) are in the typical range for $\text{N}-\text{H}\cdots\text{O}$ bonds [13]. The oxygen atoms of the $\text{N}-\text{H}\cdots\text{O}$ bonds O1 and O1* lie nearly in both planes of the equatorial ligand systems as is shown in the stereographic projection in Fig. 2. The angle between these two planes amounts to $61.25(9)^\circ$.

The Rh atoms display a distorted octahedral coordination with the $\text{dmgH}/\text{ON}=\text{C}(\text{Me})-\text{C}(\text{Me})=\text{NH}$ ligands in the equatorial plane and PPh_3 and the bromomethyl ligand in the axial positions. Whereas in other rhodoximes [2,3,5,12,14] the two dmgH^- ligands are stabilized by two strong intramolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds, complex **3a** exhibits only one $[\text{O}(2)\cdots\text{O}(3)$ 2.541(7)/2.573(8) Å]¹ and the two intermolecular $\text{N}-\text{H}\cdots\text{O}$ bridges described above. As a consequence of the strong $\text{O}-\text{H}\cdots\text{O}$ bonds the angles $\text{N}(2)-\text{Rh}-\text{N}(3)$ [$97.6(2)/97.4(3)^\circ$] are smaller than the angles $\text{N}(1)-\text{Rh}-\text{N}(4)$ [$106.7(2)/106.1(2)^\circ$].

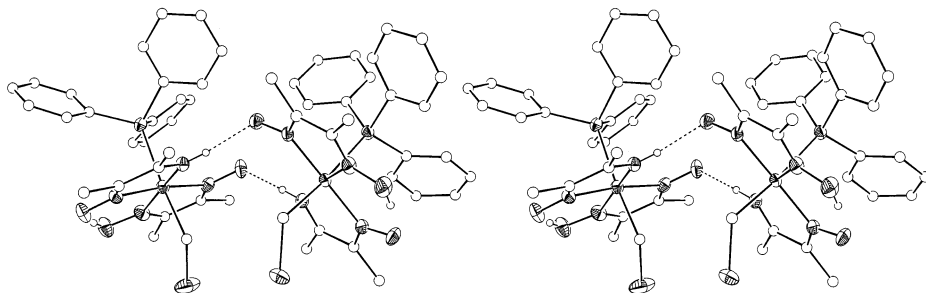
As expected, the $\text{P}-\text{Rh}-\text{C}$ unit is nearly linear [$174.7(2)/175.0(2)^\circ$]. But unexpectedly, there is a significant difference ($\Delta = 0.02$ Å) between the two $\text{Rh}-\text{P}$ bond lengths [$\text{Rh}-\text{P}$ 2.423(2)/2.443(2) Å]. Their magnitudes are in-between the $\text{Rh}-\text{P}$ bond length of the phenylalkynyl complex $[\text{Rh}]-\text{C}\equiv\text{CPh}$ [2.409(1) Å] ([15]a) and the vinyl complex $[\text{Rh}]-\text{CH}=\text{CH}_2$ [2.447(1) Å] ([15]b) pointing to a relatively low *trans* influence of the bromomethyl ligand. The $\text{Rh}-\text{C}$ bond length [$\text{Rh}-\text{C}(27)$ 2.073(6)/2.078(6) Å] corresponds to those in the mononuclear alkyl complexes $[\text{Rh}]-\text{R}$ { $\text{R} = \text{Me}$, Et; $\text{Rh}-\text{C}$ 2.064(7)/2.119(4) Å ([15]c,d)}. As in (non-re-

Table 1
Selected bond lengths (Å) and bond angles ($^\circ$) for **3a**^a

Rh–C(27)	2.073(6)/2.078(6)	C(27)–Rh–P	174.7(2)
Rh–P	2.423(2)/2.443(2)	Br–C(27)–Rh	175.0(2)
Rh–N(1)	2.022(5)/2.035(5)	N(1)–Rh–P	121.0(3)
Rh–N(2)	1.987(5)/1.983(5)	N(2)–Rh–P	121.8(3)
Rh–N(3)	2.005(5)/1.998(5)	N(3)–Rh–P	90.94(14)
Rh–N(4)	2.027(5)/2.031(5)	N(4)–Rh–P	90.18(14)
N(1)–O(1)	1.300(6)/1.309(6)	N(1)–Rh–N(2)	92.0(2)/90.9(2)
N(2)–O(2)	1.373(6)/1.369(6)	N(3)–Rh–N(4)	92.3(2)
N(3)–O(3)	1.310(6)/1.308(6)	N(1)–Rh–N(4)	95.59(14)
C(27)–Br	1.945(6)/1.920(7)	N(2)–Rh–N(3)	92.89(14)
		C(27)–Rh–N(1)	93.82(13)
		C(27)–Rh–N(2)	77.4(2)/78.3(2)
		C(27)–Rh–N(3)	78.0(2)/77.7(2)
		C(27)–Rh–N(4)	106.7(2)
			106.1(2)
			97.6(2)/97.4(3)
			83.8(2)/87.3(3)
			87.2(2)/92.8(2)
			93.0(2)/87.3(3)
			88.3(2)/82.8(2)

^a Here and as follows the first figure refers to the molecule $[\text{Rh}, \dots, \text{C}1-\text{C}27]$ and the second one to the molecule $[\text{Rh}^*, \dots, \text{C}1^*-\text{C}27^*]$.

¹ Here and as follows the first figure refers to the molecule $[\text{Rh}, \dots, \text{C}1-\text{C}27]$ and the second one to the molecule $[\text{Rh}^*, \dots, \text{C}1^*-\text{C}27^*]$.

Fig. 2. Stereographic projection for **3a**.

duced) organorhodoximes, the dm₂H and ON=C(Me)–C(Me)=NH ligands are tilted away from the triphenylphosphine ligand what can be described [16] by the angle $\alpha = 4.9(4)/9.8(3)^\circ$ between the normal vectors of the dm₂H and the ON=C(Me)–C(Me)=NH planes and by the displacement of the Rh atom out of the mean plane passing through the four N-donor atoms towards the P atom $d(\text{Rh}/\text{N}4) = 0.072(2)/0.091(2)$ Å. Similar values for α and d were found in the ‘normal’ organorhodoximes [Rh]–R (R = Me, Et, CH=CH₂, C≡CPh, $\alpha = 6.2$ – 15.1° ; $d(\text{Rh}/\text{N}4) = 0.07$ – 0.13 Å) ([15]a–d).

The relatively great differences (3.5–5.7°) (Table 1) between the angles C(27)–Rh–N and the corresponding angles C(27)*–Rh*–N* might be a result of the different orientation of the bromomethyl ligand in respect to the equatorial ligand system measured by the torsion angles Br–C(27)–Rh–N(4) (52.9(4)°) and Br*–C(27)*–Rh*–N(4)* (176.2(4)°).

2.3. NMR spectroscopy

Selected NMR data of complexes **3a–c** are summarized in Table 2. The assignment of the ¹³C and ¹H signals was proved by HETCOR experiments and attached proton test (APT) spectra.

Contrary to the non-reduced organorhodoximes [Rh]–R, all four methyl groups and all four oxime/imine groups are non-equivalent in complexes **3a–c**. The imine carbon atoms are strongly downfield shifted (C=NH 172.9–174.2 ppm vs. C=NOH 145.4–153.3 ppm). The chemical shifts of the methyl groups attached to the imine groups fall in the range $\delta_{\text{H}} = 1.99$ – 2.04 ppm and $\delta_{\text{C}} = 22.7$ – 22.8 ppm, at lower field than those of the corresponding methyl groups attached to the oxime/oximate groups ($\delta_{\text{H}} = 1.58$ – 1.84 ppm; $\delta_{\text{C}} = 10.9$ – 12.7 ppm). The same observations were made in bis(phosphin) rhodium complexes [Rh(dm₂H){ON=C(Me)–C(Me)=NH}–(PR₃)₂]X (**4**) (X = NO₃, ClO₄, [Rh(dm₂H)₂Cl₂]) [9].

The only characteristic difference in the axial moiety P–Rh–C between the reduced complexes **3a–c** and the corresponding non-reduced complexes **2a–c** is a downfield shift of the phosphorus resonances of about 3–5 ppm.

3. Discussion

There are two further reports on reduction of dimethylglyoximate complexes into oxime–imine complexes: (i) [Rh(dm₂H)(dm₂H₂)Cl₂] reacts with NaBH₄ in methanolic KOH in the presence of phosphines of small size and good donor ability to give complexes **4** (PR₃ = PEt₃, P(*n*-Bu)₃, PPh₂Me) [9]. (ii) [TcCl₃(MeCN)(PPh₃)₂] reacts with dm₂H₂ in the presence of ethylboronic acid to give not only the expected complex [TcCl{(dm₂H)₂(dm₂)BET}] but also complex **5** with an oxime–imine ligand [17]. As with complexes **3**, the mechanism of the reduction is not at all clear. In the case of the complex **4**, the assumption was made tentatively that the loss of oxime oxygen gives OH[–] [9]. In the case of complex **5** it does seem likely that the imine moiety forms at or near the time of coordination of the ligand to technetium [17].

Attempts to carry out the reaction of complexes **6** (R = CH₂Br; L = py, H₂O, *N*-methylimidazole) with NaOMe did not lead to the expected methoxymethyl complexes **6** (R = CH₂OMe) (analogous to the conversion of [Co(CH₂Br)(dm₂H)₂(py)] to [Co(CH₂OMe)(dm₂H)₂(py)] [10]) but to complex **7** with a Co–N–C three-membered cycle [11]. This demonstrates that the reduction **2** → **3** might also be enforced by a neighboring group effect. The reduction agent could be the excess of NaBH₄.

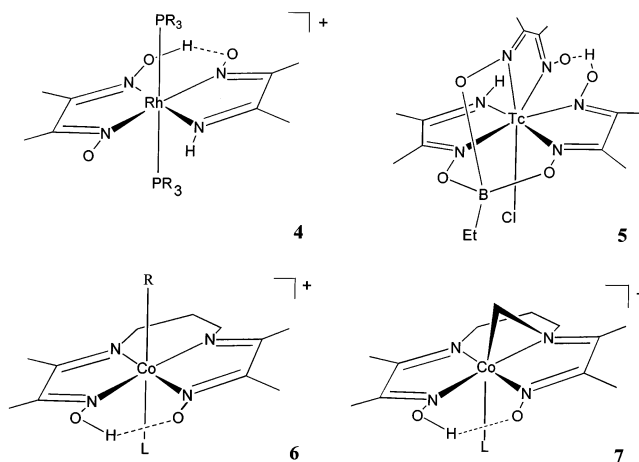


Table 2
Selected NMR data (chemical shifts in ppm, coupling constants in Hz) of complexes **3a–c** (values of the corresponding non-reduced complexes **2a–c** are given for comparison [3]a)

	3a (X = Br)	3b (X = Cl)	3c (X = OMe)
CH ₂ X			
$\delta(^{13}\text{C})$ [$^2J(\text{P,C})/^1J(\text{Rh,C})$]	38.7 [113.2/26.3]	46.6 [108.3/24.4]	80.5 [109.7/20.9] ^a
$\delta(^1\text{H})$ [$^2J(\text{Rh,H})/^3J(\text{P,H})$]	3.45 [2.2/3.5]	3.64 [2.5/3.1]	4.10 [—/2.6]
dmgH/ON=C(Me)–C(Me)=NH			
CH ₃ $\delta(^{13}\text{C})/\delta(^1\text{H})$ [$^5J(\text{P,H})$]	11.2/1.58 [1.2]	11.2/1.58 [1.2]	10.9/1.58
	11.8/1.79	11.8/1.79	11.6/1.80
	12.7/1.83 [1.2]	12.7/1.83	12.5/1.84
	22.8/2.03 [1.2]	22.7/2.04 [1.2]	22.7/1.99
C=N $\delta(^{13}\text{C})$ [$^2J(\text{Rh,C})$]	146.2 [2.2]	146.8	145.4
	150.4 [2.4]	150.3	149.7
	153.3 [2.0]	153.2	152.4
	174.2 [3.0]	174.1	172.9
NH/OH: $\delta(^1\text{H})$	10.50/4.06	10.09/4.60	15.60/10.05
PPh ₃			
$\delta(^{31}\text{P})$ [$^1J(\text{Rh,P})$]	12.7 [71.2]	13.4 [69.5]	10.7 [62.4]
	2a (X = Br)	2b (X = Cl)	2c (X = OMe)
CH ₂ X			
$\delta(^{13}\text{C})$ [$^2J(\text{P,C})/^1J(\text{Rh,C})$]	39.2 [112.6/27.1]	47.4 [107.1/25.8]	81.4 [85.5/21.2] ^b
$\delta(^1\text{H})$ [$^2J(\text{Rh,H})/^3J(\text{P,H})$]	3.30 [1.7/1.7]	3.43 [2.4/3.3]	3.94 [0.9/2.6]
dmgH			
CH ₃ $\delta(^{13}\text{C})/\delta(^1\text{H})$ [$^5J(\text{P,H})$]	11.8/1.88 [2.0]	11.7/1.87 [2.0]	11.5/1.87 [1.2]
C=N $\delta(^{13}\text{C})$	147.5	149.4	148.5
PPh ₃			
$\delta(^{31}\text{P})$ [$^1J(\text{Rh,P})$]	8.0 [70.8]	10.0 [68.4]	6.4 [59.8]

^a –OCH₃: $\delta(^1\text{H}) = 3.05$, $\delta(^{13}\text{C}) = 60.8$. ^b –OCH₃: $\delta(^1\text{H}) = 3.11$, $\delta(^{13}\text{C}) = 61.0$.

The unusual reduction described in this paper is not only of interest with respect to the stability of the bis(dimethylglyoximate) complexes that are B12 model complexes but also with respect to reductive cleavage of oximes by low-valent transition metal compounds [18].

4. Experimental

All reactions with Rh^I were carried out under argon using Schlenk techniques. [Rh]–Cl was prepared according to a published method [19]. All other chemicals were reagent grade and used without further purification. Solvents were dried and distilled prior use by standard methods. Microanalyses (C, H, N, Br) were performed by the University of Halle microanalytical laboratory using CHNS-932 (LECO) and vario EL (elementar Analysensysteme) elemental analyzer, respectively. ¹H-, ¹³C- and ³¹P-NMR spectra were recorded on Varian UNITY 500 and GEMINI 200 spectrometers operating at 499.88 and 199.97 MHz for ¹H, respectively (¹³C at 125.71/50.28 MHz, ³¹P at 202.36/80.95 MHz). Solvent signals (¹H, ¹³C) were used as internal standards; $\delta(^{31}\text{P})$ is referred to external H₃PO₄ (85%). Two-dimensional heteronuclear correla-

tion NMR spectra (HETCOR) were recorded on the UNITY 500 spectrometer. For the osmometric molecular weight determination a Vapor Pressure Osmometer no. A0280 (Knauer) was used.

4.1. [Rh(CH₂X){ON=C(Me)–C(Me)=NH}(dmgH)-(PPh₃)] (X = Br, **3a**; X = OMe, **3c**)

To a solution of [Rh]–Cl (957 mg, 1.52 mmol) in methanolic KOH (75 ml, 0.15 M), a solution of NaBH₄ (76 mg, 2.00 mmol) in methanolic KOH (25 ml, 0.15 M) was added dropwise and stirred for 2 h at 20°C to give a deep violet solution of [Rh][–]. To this CH₂Br₂ (350 mg, 2.00 mmol) in methanol (20 ml) was added within 5 min. After the color had turned to yellow (5 min), the stirring was continued for 30 min and water (100 ml) was added. After 12 h, the yellow precipitate of **3a** was filtered off, washed with diethyl ether and recrystallized from chloroform. Yield of **3a**: 475 mg (47%). Extraction of the water/methanol solution with CH₂Cl₂ afforded a mixture of complexes **2a** and **3a** (**2a**: **3a** ca. 2:1). Yield: 115 mg (12%).

3a: Anal. Found: C, 47.20; H, 4.37; Br, 12.23; N, 7.78%. Calc. for C₂₇H₃₁BrN₄O₃PRh: C, 48.23; H, 4.50; Br, 11.87; N, 8.33%. ¹³C-NMR (CDCl₃, 125 MHz): δ

129.8 ($^1J(\text{P},\text{C}) = 34.9$ Hz, C_i), 133.5 ($^2J(\text{P},\text{C}) = 10.8$ Hz, C_o), 128.2 ($^3J(\text{P},\text{C}) = 9.4$ Hz, C_m), 130.1 ($^4J(\text{P},\text{C}) = 2.3$ Hz, C_p); for further values see Table 2.

The addition of CH_2Br_2 within 3 h (instead of 5 min) afforded a mixture of complexes **3c** and **3a** (ca. 1:1) after recrystallization (three times) from chloroform. Yield: 211 mg (21%).

3c: ^{13}C -NMR (CDCl_3 , 125 MHz): δ 130.0 ($^1J(\text{P},\text{C}) = 34.9$ Hz, C_i), 133.5 ($^2J(\text{P},\text{C}) = 10.8$ Hz, C_o), 128.2 ($^3J(\text{P},\text{C}) = 9.4$ Hz, C_m), 130.1 ($^4J(\text{P},\text{C}) = 2.3$ Hz, C_p); for further values see Table 2.

4.2. $[\text{Rh}(\text{CH}_2\text{Cl})\{\text{ON}=\text{C}(\text{Me})-\text{C}(\text{Me})=\text{NH}\}(\text{dmgH})-(\text{PPh}_3)]$ (**3b**)

To a solution of $[\text{Rh}]^-$ (1.52 mmol) in methanolic KOH (100 ml, 0.15 M), prepared as described above, CH_2Cl_2 (175.0 mg, 2.00 mmol) in methanol (20 ml) was added within 5 min. After the color had turned to yellow (2.5 h), the stirring was continued for 30 min and water (100 ml) was added. After 12 h, the yellow precipitate was filtered off, washed with diethyl ether and dried in vacuo. Yield of the crude product (**3b:2b** ca. 1:1): 86 mg (10%). Recrystallization (four times) from acetone/heptane afforded **3b:2b** (ca. 4:1). Yield: 44 mg (5%).

Extraction of the water/methanol solution with CH_2Cl_2 afforded complex **2b** as main product. Yield: 380 mg (39%).

3b: ^{13}C -NMR (CDCl_3 , 125 MHz): δ 130.1 ($^1J(\text{P},\text{C}) = 33.9$ Hz, C_i), 133.5 ($^2J(\text{P},\text{C}) = 10.8$ Hz, C_o), 128.2 ($^3J(\text{P},\text{C}) = 9.5$ Hz, C_m), 130.1 (s, C_p); for further values see Table 2.

4.3. Crystallographic studies

Suitable single crystals of **3a** were obtained by recrystallization from chloroform. The X-ray measurement was performed on a STOE IPDS image plate system. For the measurement the reciprocal space has been scanned with 133 frames each of which oscillating the crystal 1.5° around the φ -axis.

Crystal data collections and processing parameters are listed in Table 3. The structure was solved with direct methods (SHELXS-86 [20]) and subsequent Fourier difference synthesis revealed the positions of all non-H atoms which were refined with anisotropic displacement parameters by full-matrix least-squares routines against F^2 (SHELXL-93 [21]). Hydrogen atoms were placed in calculated positions and refined isotropically with fixed displacement parameters (riding model).

5. Supplementary material available

Further details of the crystal structure analysis are

Table 3

Crystal data collection and processing parameters for **3a**

Molecular formula	$\text{C}_{27}\text{H}_{31}\text{BrN}_4\text{O}_3\text{PRh}$
<i>M</i>	673.35
Color	Yellow
Size (mm^3)	$0.2 \times 0.2 \times 0.1$
<i>T</i> (K)	298(2)
Crystal system	Triclinic
Space group	$P\bar{1}$
<i>a</i> (Å)	11.900(2)
<i>b</i> (Å)	12.850(2)
<i>c</i> (Å)	20.946(4)
α (°)	105.386(14)
β (°)	91.417(14)
γ (°)	109.72(2)
<i>V</i> (Å ³)	2883.8(8)
<i>Z</i>	4
λ_0 (Å)	0.71073 (Mo–K $_{\alpha}$ radiation)
<i>D</i> _{calc.} (g cm^{-3})	1.551
μ (mm^{-1})	2.068
<i>F</i> (000)	1360
θ range (°)	1.76–24.02
No. reflections collected	16710
No. independent reflections	8534
<i>R</i> _{int}	0.0747
No. reflections with $[I > 2\sigma(I)]$	5516
Data/restraints/parameters	8533/0/667
Final <i>R</i> ₁ , <i>wR</i> ₂ [$I > 2\sigma(I)$] ^a	0.0491, 0.0988
All data	0.0947, 0.1157
GOF (<i>S</i>) ^b	0.998
Largest residual peaks (e Å^{-3})	0.927, −0.629

^a $R_1 = \Sigma \|F_o| - |F_c| \| / \Sigma |F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{0.5}$.

^b *S* (goodness-of-fit) = $[\Sigma w(F_o^2 - F_c^2)^2 / (N_{\text{obs}} - N_{\text{param}})]^{0.5}$ (based on all data)

available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository no. CCDC-100963, the names of the authors, and the journal citation.

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References

- [1] J.H. Weber, G.N. Schrauzer, J. Am. Chem. Soc. 92 (1970) 726.
- [2] (a) R. Dreos Garlatti, G. Tauzher, G. Costa, Inorg. Chim. Acta 121 (1986) 27. (b) B. Giese, J. Hartung, C. Kesselheim, H.J. Lindner, I. Svoboda, Chem. Ber. 126 (1993) 1193. (c) F. Asaro, R. Dreos Garlatti, G. Pellizer, G. Tauzher, Inorg. Chim. Acta 211 (1993) 27. (d) F. Asaro, G. Costa, R. Dreos, G. Pellizer, W. von Philipsborn, J. Organomet. Chem. 513 (1996) 193.

- [3] (a) D. Steinborn, M. Ludwig, J. Organomet. Chem. 463 (1993) 65. (b) A.M.A. Aisa, F.W. Heinemann, D. Steinborn, Z. Anorg. Allg. Chem. 622 (1996) 1946. (c) D. Steinborn, L. Yang, A.M.A. Aisa, J. Organomet. Chem. 526 (1996) 43. (d) M. Ludwig, L. Öhrström, D. Steinborn, Magn. Reson. Chem. 33 (1995) 984.
- [4] (a) D. Steinborn, M. Rausch, C. Bruhn, H. Schmidt, D. Ströhl, J. Chem. Soc. Dalton Trans. (1998) 221. (b) M. Rausch, C. Bruhn, D. Steinborn, Proc. 16th Conf. Coord. Chem. Smolenice/Bratislava, 1997, 153.
- [5] D. Steinborn, A.M.A. Aisa, F.W. Heinemann, S. Lehmann, J. Organomet. Chem. 527 (1997) 239.
- [6] R. Dreos Garlatti, G. Tauher, M. Blaschich, G. Costa, Inorg. Chim. Acta 105 (1985) 129.
- [7] F. Asaro, R. Dreos, S. Geremia, et al., J. Organomet. Chem. 525 (1996) 71.
- [8] F.W. Heinemann, A.M.A. Aisa, D. Steinborn, Z. Kristallogr. 211 (1996) 837.
- [9] R. Dreos, G. Tauher, S. Geremia, et al., Inorg. Chem. 33 (1994) 5404.
- [10] G.N. Schrauzer, A. Ribeiro, L.P. Lee, R.K.Y. Ho, Angew. Chem. 83 (1971) 849.
- [11] S.M. Polson, L. Hanson, L.G. Marzilli, J. Am. Chem. Soc. 118 (1996) 4804.
- [12] T. Ramasami, J.H. Espenson, Inorg. Chem. 19 (1980) 1846.
- [13] A.F. Wells, Structural Inorganic Chemistry, 5th ed, Clarendon Press, Oxford, 1993, p. 357.
- [14] N. Bresciani Pahor, R. Dreos-Garlatti, S. Geremia, L. Randaccio, G. Tauher, E. Zangrando, Inorg. Chem. 29 (1990) 3437.
- [15] (a) M. Dunaj-Jurco, V. Kettmann, D. Steinborn, M. Ludwig, Acta Crystallogr. Sect. C 51 (1995) 210. (b) M. Dunaj-Jurco, V. Kettmann, D. Steinborn, M. Ludwig, Acta Crystallogr. Sect. C 50 (1994) 1427. (c) I. Potocnak, M. Dunaj-Jurco, M. Ludwig, D. Steinborn, Acta Crystallogr. Sect. C 51 (1995) 1999. (d) M. Dunaj-Jurco, V. Kettmann, D. Steinborn, M. Ludwig, Acta Crystallogr. Sect. C 50 (1994) 1239.
- [16] (a) N. Bresciani Pahor, M. Forcolin, L.G. Marzilli, L. Randaccio, M.F. Summers, P.J. Toscano, Coord. Chem. Rev. 63 (1985) 1. (b) L. Randaccio, N. Bresciani Pahor, E. Zangrando, Chem. Soc. Rev. 18 (1989) 225.
- [17] K.E. Linder, D.P. Nowotnik, M.F. Malley, J.Z. Gougoutas, A.D. Nunn, Inorg. Chim. Acta 190 (1991) 249.
- [18] T. Gilchrist, in: B. Trost, I. Flemming (Eds.), Comprehensive Organic Synthesis, vol. 8, Pergamon Press, Oxford, 1991, p. 381.
- [19] P. Powell, J. Chem. Soc. (A) (1969) 2418.
- [20] G.M. Sheldrick, SHELXS-86, Program for the Solution of Crystal Structures, University of Göttingen, Germany, 1986.
- [21] G.M. Sheldrick, SHELXL-93, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1993.