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Metal-mediated hydrolysis of the oxime C=N bond to produce Rh^{III}-bound O-iminoacylated $MeC(=NH)ONH_2$ species

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Received 21st February 2000, Accepted 28th March 2000
Published on the Web 27th April 2000

Reaction of the acetonitrile complex $[RhCl_3(MeCN)_3]$ with 2-propanone oxime, $Me_2C=NOH$, or, alternatively, interaction of $[RhCl_3(Me_2C=NOH)_3]$ and acetonitrile led to the formation of two rhodium(III) products that contain newly formed chelated iminoacyl ligands, *i.e.* $[RhCl_3\{NH=C(Me)ON=CMe_2\}(HON=CMe_2)]$ **1** and $[RhCl_2\{NH=C(Me)ON=CMe_2\}_2]Cl$ **2**. Complex **1** can be transformed to **2** by further reaction with acetonitrile. Metathesis of **2** and $Na[SbF_6]$ in water gave $[RhCl_2\{NH=C(Me)ON=CMe_2\}_2][SbF_6]$ **3** that was structurally characterized by single-crystal X-ray diffraction. In 0.1 M HCl, **2** is subject to a facile stepwise hydrolysis of the two usually stable oxime C=N bonds giving $[RhCl_3\{NH=C(Me)ON=CMe_2\}\{NH=C(Me)ONH_2\}]Cl\cdot H_2O$ **4**, as the monohydrolysed product, and ultimately furnished $[RhCl_2\{NH=C(Me)ONH_2\}_2]Cl$ **5** that was characterized by X-ray diffraction. The latter complex can be converted into **2** on prolonged refluxing in an acetone–ethanol mixture.

Introduction

Although hydroxylamine is an ambidentate nucleophile, in the overwhelming majority of cases it adds to RC≡N *via* its nitrogen and this reaction leads to generation of amide oximes, $RC(NH_2)=NOH$.[1] Such additions of NH_2OH to C≡N groups are used both in the laboratory and in industry in the production of (*i*) polymers containing $C(NH_2)=NOH$ functionalities that, in turn, are applied for extraction of heavy-metal ions from aqueous solutions[2–4] and (*ii*) amide oximes of pharmaceutical interest.[5] Thus it is not surprising that the additions at N are well studied in organic chemistry and many of their applications are described in detail. The opposite holds true for the less usual additions at O. Indeed, it is only reported that electron-acceptor substituents R in RC≡N make the nitrile carbon increasingly susceptible to nucleophilic attack by the more electronegative oxygen, rather than by the nitrogen atom of NH_2OH, and conventional additions at N are accompanied by additions at O giving, in the latter case, carboxamides $RC(=O)NH_2$ along with NH_3 and N_2.[6] In fact, O-iminoacylated species $RC(=NH)ONH_2$ that, in principle, may arise from the O-addition of NH_2OH to organonitriles are yet unknown.

In co-ordination chemistry, reactions of amines or other nucleophiles with co-ordinated organonitriles is an area of special attention and the additions of a great number of N-donor ligands containing sp^2 and sp^3 donor atoms were observed.[7] Despite that, reactions of NH_2OH and metal-bound nitriles are yet unreported and it is unknown whether hydroxylamine could behave as a N- or O-nucleophile towards the carbon in [M]–N≡CR species. In this context, attention should be drawn to the works on the additions of substituted hydroxylamines. Thus, Wieghardt *et al.*[8] discovered the addition of monomethylhydroxylamine *via* N to MeCN in a molybdenum-promoted reaction, while McDonell *et al.*[9] observed dealkylation of Et_2NOH followed by the addition at N of acetonitrile in a tungsten-mediated process. In contrast to these observations, indicating the high nucleophilic affinity of the N atom of the substituted hydroxylamines, we recently observed additions at O of R_2NOH to MeCN bound to platinum(IV) ion,[10] which proceed similarly to reactions of nitrile metal compounds with oximes described recently by us.[11–15] It is worthwhile to mention that our attempts to react unsubstituted NH_2OH with nitriles bound to Pt^{IV}, Pt^{II}, Re^{IV} and Rh^{III} failed due to both reduction of the metal centres and some other uncontrolled processes that accompanied the interaction.

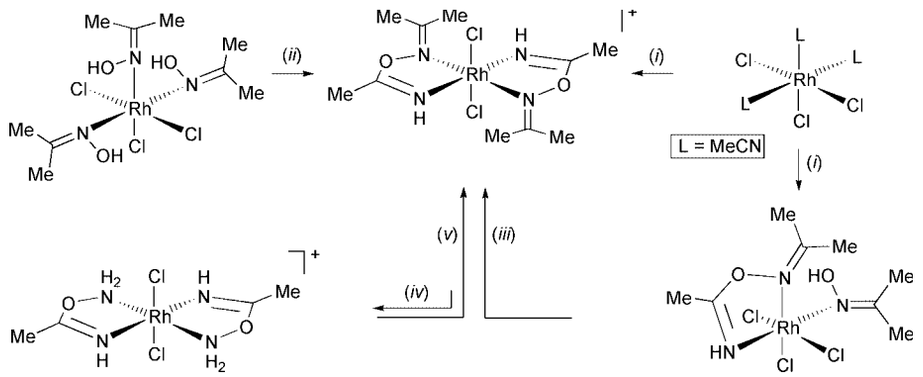
Recently we reported on the coupling between (organonitrile)rhodium(III) species and cyclopentanone oxime[15] (this reaction is now extended to 2-propanone oxime) to generate complexes containing the Rh{NH=C(R)ON=CR′R″} moiety. We now indicate a route to generate the new O-iminoacylated species $RC(=NH)ONH_2$ [or (alkylideneaminooxy)imines] which were unreachable by direct reaction of organonitrile metal complexes and NH_2OH. The suggested route involves selective metal-mediated hydrolysis of the oxime C=N bond in the Rh{NH=C(R)ON=CR′R″} unit (in which the imino group is protected, towards hydrolysis, by the metal site) and these results are given below.

Results and discussion

Coupling of 2-propanone oxime and acetonitrile

We have recently reported on a rhodium(III)-mediated coupling of organonitriles in $[RhCl_3(RCN)_3]$ (R = Me or Ph) and cyclopentanone oxime giving chelated iminoacylated ligands $NH=C(Me)ON=C(C_4H_8)$ bound to the Rh.[15] As an extension of that work we have now studied similar transformations involving 2-propanone oxime, $Me_2C=NOH$, and $[RhCl_3(MeCN)_3]$. Despite some deviations from the previous synthetic procedures relevant mostly to solubilities of starting materials

DOI: 10.1039/b001384f



Scheme 1 Observed transformations of the rhodium(III) complexes: (*i*) Me_2C=NOH in EtOH; (*ii*) and (*iii*) MeCN; (*iv*) water; (*v*) Me_2CO, reflux.

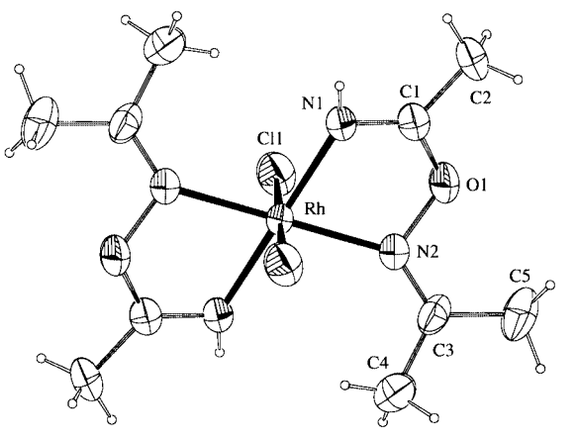


Fig. 1 A PLATON[16] drawing of $[RhCl_2\{NH{=}C(Me)ON{=}CMe_2\}_2]^+$ with the atomic numbering scheme.

Table 1 Bond lengths (Å) and angles (°) for $[RhCl_2\{NH{=}C(Me)ON{=}CMe_2\}_2]^+$ **3**

Rh–Cl(1)	2.3220(18)	N(1)–C(1)	1.270(8)
Rh–N(2)	2.032(5)	N(2)–C(3)	1.267(8)
Rh–N(1)	2.018(5)	C(1)–C(2)	1.480(9)
O(1)–N(2)	1.448(7)	C(3)–C(4)	1.487(11)
O(1)–C(1)	1.342(8)	C(3)–C(5)	1.498(10)
Cl(1)*–Rh–N(1)*	91.93(15)	N(2)–Rh–N(2)*	180.00
Cl(1)*–Rh–N(2)*	88.10(17)	N(1)*–Rh–N(2)*	77.1(2)
Cl(1)–Rh–N(1)	91.93(15)	N(2)–O(1)–C(1)	110.9(5)
Cl(1)–Rh–N(2)	88.10(17)	Rh–N(1)–C(1)	115.5(4)
Cl(1)–Rh–Cl(1)*	180.00	O(1)–N(2)–C(3)	110.9(5)
Cl(1)–Rh–N(1)*	88.07(15)	Rh–N(2)–C(3)	138.8(5)
Cl(1)–Rh–N(2)*	91.90(17)	Rh–N(2)–O(1)	110.3(4)
N(1)–Rh–N(2)	77.1(2)	O(1)–C(1)–C(2)	112.8(6)
Cl(1)*–Rh–N(1)	88.07(15)	N(1)–C(1)–C(2)	127.7(6)
N(1)–Rh–N(1)*	180.00	O(1)–C(1)–N(1)	119.5(6)
N(1)–Rh–N(2)*	102.9(2)	N(2)–C(3)–C(5)	122.9(7)
Cl(1)*–Rh–N(2)	91.90(17)	C(4)–C(3)–C(5)	118.0(7)
N(1)*–Rh–N(2)	102.9(2)	N(2)–C(3)–C(4)	119.1(6)

Symmetry transformations used to generate equivalent atoms: * $-x$, $-y+1$, $-z+1$.

and final complexes, it is not very surprising that reactions studied in the current work led to compounds of the same type as had been described (routes (*i*) and (*ii*) in Scheme 1).

Hence, in accord with the previous work,[15] it has been found that the reaction of $[RhCl_3(MeCN)_3]$ and 2-propanone oxime results in the formation of two products bearing newly formed iminoacylated ligands, *i.e.* $[RhCl_3\{NH{=}C(Me)ON{=}CMe_2\}(HON{=}CMe_2)]$ and $[RhCl_2\{NH{=}C(Me)ON{=}CMe_2\}_2]Cl$. However, in addition to the early observations,[15] it was established that the former compound can easily be converted into the latter one, formed upon a further acetonitrile–oxime coupling, on heating in MeCN (route (*iii*) in Scheme 1). Most likely, one of the main driving forces for the formation of $[RhCl_3\{NH{=}C(Me)ON{=}CMe_2\}(HON{=}CMe_2)]$ is the low solubility of this complex resulting in its precipitation from the reaction mixture thus preventing further reaction with acetonitrile.

The crystal structure of the hexafluoroantimonate salt $[RhCl_2\{NH{=}C(Me)ON{=}CMe_2\}_2][SbF_6]$, obtained by metathetical reaction of $[RhCl_2\{NH{=}C(Me)ON{=}CMe_2\}_2]Cl$ and $Na[SbF_6]$, was determined by X-ray single-crystal diffraction (Fig. 1). As expected, the co-ordination polyhedron and geometrical parameters (Table 1) of $[RhCl_2\{NH{=}C(Me)ON{=}CMe_2\}_2]^+$ resemble in all details those for the previously described complexes $[RhCl_2\{NH{=}C(R)ON{=}C(C_4H_8)\}_2]Cl$ (R = Me or Ph).[15]

Hydrolysis of $[RhCl_2\{NH{=}C(Me)ON{=}CMe_2\}_2]Cl$ (reaction (*iv*) in Scheme 1)

This was performed in 0.1 M HCl in D_2O at 80 °C and monitored by ^1H NMR spectroscopy. In the course of the reaction, the starting material [δ 2.56 (s, CH_3 **A**), 2.61 and 2.74 (two s, CH_3 **B** and **C**), (*a*) in Fig. 2] completely disappeared within 36 h and four singlets of equal intensity emerged in the spectrum. Three of these signals [δ 2.53 (CH_3 **D**), 2.60 and 2.74 (two s, CH_3 **E** and **F**)] appear close to the signals of the starting material and indicate that one NH=C(Me)ON=CMe_2 ligand

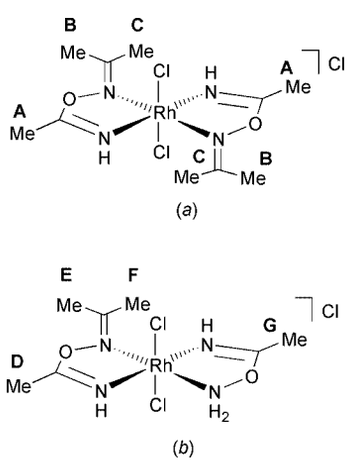


Fig. 2 The starting material (*a*) and monohydrolysed complex (*b*).

remains intact. The chemical shift of the fourth signal [δ 2.45 (CH_3 **G**)] is similar to those typically observed for methyl groups of the type HN=C(Me),[15] giving indirect evidence that in the second ligand the iminoacyl unit is still preserved, whereas the oxime C=N bond was hydrolysed [(*b*) in Fig. 2]. Concomitant formation of acetone (δ 2.22), as the other product of the hydrolysis, was detected only in the beginning of the experiment, while after a few hours this signal became considerably broadened and lost its intensity due to well known deuteriation by D_2O under the acidic conditions applied.[17] On prolonged heating of the sample (80 °C, 4 weeks) the signals of the monohydrolysed complex $[RhCl_2\{NH{=}C(Me)ON{=}CMe_2\}\{NH{=}C(Me)ONH_2\}]^+$, the first detected product of hydrolysis,

disappeared to give two singlets due to $[RhCl_2\{NH{=}C(Me)ONH_2\}_2]^+$ (δ 2.40) (see below) and acetic acid (δ 2.11), among a significant amount of low intensity signals due to unidentified by-products. The hydrolysis was also performed in D_2O and the general observations are similar to those described for the reaction in the acidic medium. However, the reaction in D_2O is faster and gives many more unidentified products. Thus, conversion of the starting material into the monohydrolysed compound (*b*) and acetone is complete after 15 h, while the further reaction to give $[RhCl_2\{NH{=}C(Me)ONH_2\}_2]Cl$ takes one week.

We succeeded in isolation of the two products from the hydrolysis. On performing the hydrolysis of $[RhCl_2\{NH{=}C(Me)ON{=}CMe_2\}_2]Cl$ in 0.1 M HCl for 36 h followed by *fast* evaporation of the solvent in vacuum at *ca.* 40 °C the intermediate (*b*) [Fig. 2], *i.e.* $[RhCl_2\{NH{=}C(Me)ON{=}CMe_2\}\{NH{=}C(Me)ONH_2\}]Cl{\cdot}H_2O$, was obtained and characterized by elemental analyses, FAB^+-MS, IR, ^1H and ^{13}C-$\{^1H\}$ NMR spectroscopies. Redissolution of the latter complex in D_2O gave the same NMR spectrum as was monitored during the reaction. However, it should be pointed out that formation of the monohydrolysed product with the protonated amine group, *i.e.* $[RhCl_3\{NH{=}C(Me)ON{=}CMe_2\}\{NH{=}C(Me)ONH_3^+Cl^-\}]$, cannot be ruled out.

When the evaporation of the reaction mixture was *slow* (3 d, room temperature) we also obtained a broad spectrum of unidentified products containing some crystalline material. The FAB^+-MS spectrum of the mixture showed peaks centred at *m*/*z* 391 and 321, which are ascribed to $[RhCl_4\{NH{=}C(Me)ONH_3\}_2]^+$ and $[RhCl_2\{NH{=}C(Me)ONH_2\}_2]^+$ complexes, along with a significant number of unattributed peaks. The crystalline product was studied by X-ray crystallography and formulated as $[RhCl_2\{NH{=}C(Me)ONH_2\}_2]Cl$ (see below). The yield of that complex was very low and the reaction, carried out at pH 1 cannot be recommended as a preparative one. Careful control and variation of the reaction conditions, however, allowed us to isolate the individual compound $[RhCl_2\{NH{=}C(Me)ONH_2\}_2]Cl$ in 24% yield (see Experimental section).

It is worthwhile to mention that the hydrolysis of the oxime C=N bond was also performed (in NMR tube, D_2O) for $[RhCl_2\{NH{=}C(Me)ON{=}C(C_4H_8)_2\}_2]Cl$ prepared in the previous study.[15] ^1H NMR monitoring of the reaction over a period of two days showed a slow disappearance of the initial HN=C(*Me*) signal at δ 2.56 with formation of two new singlets of equal intensity at δ 2.51 and 2.45, which may conditionally be attributed to the corresponding monohydrolysed product, and one singlet at δ 2.40 due to $[RhCl_2\{NH{=}C(Me)ONH_2\}_2]^+$.

Condensation of $[RhCl_2\{NH{=}C(Me)ONH_2\}_2]Cl$ and acetone

Condensations of ketones and metal-bound amines[18] (including hydroxylamine[19,20]) are known although scarce. We attempted to conduct the formally reverse reaction, *i.e.* condensation of the $NH{=}C(Me)ONH_2$ ligands in $[RhCl_2\{NH{=}C(Me)ONH_2\}_2]Cl$ with acetone. Refluxing an acetone–ethanol mixture (the latter solvent was added to increase the solubility) for 20 h gave two products which are $[RhCl_2\{NH{=}C(Me)ON{=}CMe_2\}_2]Cl$ and the monohydrolysed intermediate $[RhCl_2\{NH{=}C(Me)ON{=}CMe_2\}\{NH{=}C(Me)ONH_2\}]^+$ in approximately 7:3 ratio obtained by integration of peaks in the ^1H NMR spectrum.

Crystal structure of $[RhCl_2\{NH{=}C(Me)ONH_2\}_2]Cl$

The elemental cell contains two crystallographically independent molecules of the complex whose geometric parameters only vary within less than 3σ. The co-ordination polyhedron of $[RhCl_2\{NH{=}C(Me)ONH_2\}_2]^+$ is a slightly distorted octahedron and the rhodium atom is at the centre of symmetry (Fig. 3). The Rh–Cl bonds [2.3284(10) and 2.3270(10) Å for two crystallographically independent molecules, Table 2] agree well with the reported data for the rhodium(III) complexes $[RhCl_2(dmg)_2]^-$[21]

Table 2 Bond lengths (Å) and angles (°) for one independent molecule of $[RhCl_2\{NH{=}C(Me)ONH_2\}_2]Cl$ **5**

Rh(2)–Cl(1)	2.3284(10)	O(2)–C(3)	1.350(5)
Rh(2)–N(3)	2.006(3)	N(3)–C(3)	1.264(5)
Rh(2)–N(4)	2.025(3)	C(3)–C(4)	1.489(7)
O(2)–N(4)	1.473(4)		
Cl(1)–Rh(2)–N(3)	92.17(10)	N(4)–Rh(2)–N(4′)	180.00
Cl(1)–Rh(2)–N(4)	90.39(10)	Cl(1′)–Rh(2)–N(3′)	92.17(10)
Cl(1)–Rh(2)–Cl(1′)	180.00	Cl(1′)–Rh(2)–N(4′)	90.39(10)
Cl(1)–Rh(2)–N(3′)	87.83(10)	N(3′)–Rh(2)–N(4′)	78.52(14)
Cl(1)–Rh(2)–N(4′)	89.61(10)	N(4)–O(2)–C(3)	112.3(3)
N(3)–Rh(2)–N(4)	78.52(14)	Rh(2)–N(3)–C(3)	117.1(3)
Cl(1′)–Rh(2)–N(3)	87.83(10)	Rh(2)–N(4)–O(2)	111.8(2)
N(3)–Rh(2)–N(3′)	180.00	N(3)–C(3)–C(4)	127.7(4)
N(3)–Rh(2)–N(4′)	101.48(14)	O(2)–C(3)–N(3)	119.7(4)
Cl(1′)–Rh(2)–N(4)	89.61(10)	O(2)–C(3)–C(4)	112.6(4)
N(3′)–Rh(2)–N(4)	101.48(14)		

[a] Symmetry transformations used to generate equivalent atoms: ′1 $-x$, $-y$, $-z$.

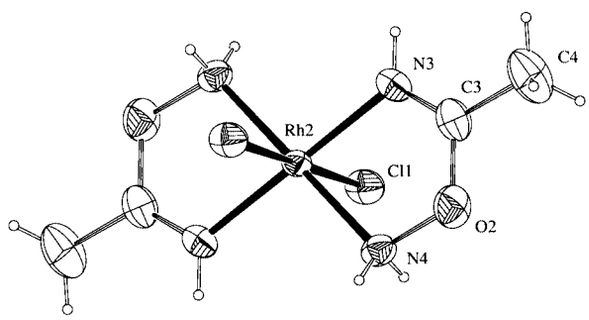


Fig. 3 A PLATON drawing of $[RhCl_2\{NH{=}C(Me)ONH_2\}_2]^+$ with the atomic numbering scheme.

(dmg = monodeprotonated dimethylglyoxime) [average 2.34 Å] and $[RhCl_2(HONCH_2CH_2NOH)(HONCH_2CH_2NO)]$ [average 2.33 Å[22]], although these complexes have different overall charges. In addition, it corresponds to the Rh–Cl distance in the $[RhCl_2\{NH{=}C(R)ON{=}CR'R''\}_2]^+$ [average 2.33 Å] complexes reported by us.[15] The five membered chelated ring Rh(2)-N(3)C(3)O(2)N(4) is close to planar with the following mean deviations from the least-squares plane: Rh(2) 0.0495(14), N(3) −0.032(4), C(3) 0.002(4), O(2) 0.029(3), N(4) −0.049(4) Å. The two chelated ligands are mutually *trans* and bound to the rhodium(III) centre through amino and imino nitrogens. The conversion of the $NH{=}C(Me)ON{=}CMe_2$ ligand into the $NH{=}C(Me)ONH_2$ one did not lead to significant changes within the chelated ring.

The NH_2 group is involved in two different types of hydrogen bridges, one to the chloride counter ion [N(2)–H···Cl(3) distances are 0.88(4) and 2.40(4) Å, angle is 153(4)°, N(4)–H···Cl(3) distances are 0.84(5) and 2.49(5) Å, angle is 168(5)°] and another one to the co-ordinated chloride of the neighbouring complex [N(2)–H···Cl(1) 0.89(4) and 2.32(4) Å, angle 153(4)°; N(4)–H···Cl(2) 0.73(4) and 2.49(4) Å, angle 173(4)°], while the imino NH group only forms hydrogen bridges to the Cl^- counter ion [N(1)–H···Cl(3) distances are 0.68(5) and 2.52(5) Å, angle is 162(5)°, N(3)–H···Cl(3) distances are 0.82(5) and 2.43(5) Å, angle is 171(4)°].

Concluding remarks

We believe that the hydrolysis is metal-mediated on the basis of the following reasons: (*i*) the stepwise character of the hydrolysis observed in the ^1H NMR experiment indicates that, in general, co-ordination affects the reaction; (*ii*) it is well documented that direct hydrolysis of oximes to carbonyl compounds and NH_2OH is very slow and, therefore, requires harsh reaction conditions and is subject to side processes (usual

methods of cleavage of the oxime C=N double bond involve either oxidation or reduction of the oxime nitrogen);[18,23] (*iii*) the hydrolysis is faster in water than in acidic media, while the opposite holds true for free oximes; (*iv*) in organic compounds the imino group is much more sensitive towards hydrolysis than the oxime one;[24] (*v*) recently we observed a facile addition of ketoximes, aldoximes, amidoximes and chloroximes to platinum(IV)–nitrile complexes[10–12] giving monodentate ligands bound to Pt^{IV}, *e.g.* [Pt^{IV}]–NH=C(R)ON=CR′R″, with a peripheral oxime part that was shown to be exceptionally stable towards hydrolysis.

Hence, the rhodium(III) metal centre of this study stabilizes the usually unstable imino group towards hydrolysis, whereas it selectively promotes this type of reaction for the commonly stable oxime group. The generality of such an unprecedented role of a metal site will be tested for other metals.

Experimental

Materials and instrumentation

2-Propanone oxime (Aldrich), $RhCl_3·4H_2O$ (Reakhim) and solvents were obtained from commercial sources and used as received; [$RhCl_3(MeCN)_3$] was prepared in accord with the published method.[25] C, H and N elemental analyses were carried out by Microanalytical Services of the Instituto Superior Técnico. Melting and/or decomposition points were determined on a Kofler table. Positive-ion FAB mass spectra were obtained on a Trio 2000 instrument by bombarding 3-nitrobenzyl alcohol (NBA) matrices of samples with 8 keV (*ca.* 1.28×10^{15} J) Xe atoms. Mass calibration for data system acquisition was achieved using CsI. Infrared spectra (4000–400 cm^{-1}) were recorded on a Bio-Rad FTS 3000 MX instrument in KBr pellets, ^1H and ^{13}C-{^1H} NMR spectra on a Varian UNITY 300 spectrometer at ambient temperature.

Synthetic work and characterization

***mer*-[$RhCl_3(Me_2C{=}NOH)_3$].** Oxime (1.24 mmol) was added at 20–25 °C to a solution of $RhCl_3·4H_2O$ (0.10 g, 0.36 mmol) in EtOH (3 mL). The homogeneous dark red reaction mixture formed was heated at 70 °C for 5 min until it turned to dark orange, then cooled to room temperature. A crystalline yellow precipitate was released on stirring the solution with a glass stick. This was then left at 20–25 °C for 12 h, collected on a filter, washed with two 3 mL portions of EtOH and three 3 mL portions of Et_2O and dried in air at room temperature. Yield 0.08 g, 50%. Found: C, 25.2; H, 4.8; N, 9.6%. $C_9H_{21}Cl_3N_3O_3Rh$ requires C, 25.2; H, 4.9; N, 9.8%. mp = 193 °C (decomp.). FAB$^+$-MS: *m*/*z* 392, $[M - Cl]^+$; 356, $[M - 2Cl - H]^+$; and 320, $[M - 3Cl - 2H]^+$. IR spectrum, cm^{-1} (selected bands): 3338 and 3256vs (br) *ν*(O–H), 1648m *ν*(C=N) and 1267s *δ*(OH). The complex is unstable in both EtOH (TLC monitoring) and CD_3OD (^1H NMR monitoring) giving on standing at *ca.* 50 °C a large variety of unidentified products. ^1H NMR spectrum in $CDCl_3$: *δ* 2.31 (s, 3H), 2.32 (s, 6H), 2.41 (s, 3H), 2.44 (s, 6H), 9.38 (s, br, 1H) and 9.40 (s, br, 2H). ^{13}C-{^1H} NMR spectrum in $CDCl_3$: *δ* 21.1 ($1CH_3$), 21.5 ($2CH_3$), 24.1 ($1CH_3$), 24.8 ($2CH_3$), 173.8 (2C=N) and 174.2 (1C=N).

Iminoacylation in the reaction between *mer*-[$RhCl_3(MeCN)_3$] and Me_2C=NOH in ethanol. The complex *mer*-[$RhCl_3(MeCN)_3$] (0.20 g, 0.60 mmol) was dissolved in hot (70 °C) ethanol (5 mL), 2-propanone oxime (0.10 g, 1.37 mmol) added and the reaction mixture heated at 70 °C for 3 min until it turned from dark to pale orange. The solution was stirred at 20–25 °C for 20 h, whereafter an orange precipitate was collected on a filter, washed with three 3 mL portions of ethanol, three 3 mL portions of chloroform and three 3 mL portions of diethyl ether and dried in air at room temperature. Yield of [$RhCl_3${NH=C(Me)ON=CMe_2}(HON=CMe_2)] **1** 0.030 g (13%). The filtrate was then heated at 60 °C for 4 h, the solvent removed *in vacuo* at room temperature to give an oily residue. The addition of chloroform (3 mL), filtration from some insoluble material (*ca.* 15 mg) and addition of diethyl ether gave a precipitate that was filtered off and dried in air at room temperature. Yield of crude [$RhCl_2${NH=C(Me)ON=CMe_2}$_2$]Cl **2** 0.10 g, 38%. The product can be recrystallized from ethanol. However, much more pure material can be obtained by the reaction of *mer*-[$RhCl_3(Me_2C{=}NOH)_3$] and acetonitrile (see below).

[$RhCl_3${NH=C(Me)ON=CMe_2}(HON=CMe_2)]. Found: C, 24.1; H, 4.3; N, 10.4%. $C_8H_{17}Cl_3N_3O_2Rh$ requires C, 24.2; H, 4.3; N, 10.6%. mp = 242 °C (decomp.). FAB$^+$-MS: *m*/*z* 395, [$RhCl_3${NH=C(Me)ON=CMe_2}(HON=CMe_2)]$^+$. IR spectrum, cm^{-1} (selected bands): 3219s (br) *ν*(O–H), 1682s and 1633m *ν*(C=N), 1189 *ν*(C–O). ^1H NMR spectrum in DMSO-d_6: *δ* 2.45, 2.47, 2.53, 2.57 and 2.71 (s, 3H each, 5 Me), 8.86 (s, br, 1H, NH) and 9.38 (s, 1H, OH); NH was not detected. The compound is insoluble in most common deuteriated solvents. In DMSO-d_6 it is not sufficiently stable to give a ^{13}C-{^1H} NMR spectrum.

[$RhCl_2${NH=C(Me)ON=CMe_2}$_2$]Cl. Found: C, 27.6; H, 5.0; N, 12.7%. $C_{10}H_{20}Cl_3N_4O_2Rh$ requires C, 27.4; H, 4.7; N, 12.8%. mp = 205 °C (decomp.). FAB$^+$-MS: *m*/*z* 401, [$RhCl_2${NH=C(Me)ON=CMe_2}$_2$]$^+$. IR spectrum, cm^{-1} (selected bands): 1681 and 1641 *ν*(C=N), 1194 *ν*(C–O). ^1H NMR spectrum in D_2O: *δ* 2.56 (s, 3H), 2.61 (s, 3H) and 2.74 (s, 3H). ^{13}C-{^1H} NMR spectrum in D_2O: *δ* 17.1 ($1CH_3$), 24.1 ($1CH_3$), 26.7 ($1CH_3$) 175.7 (C=N) and 186.1 (C=N). The complex gave pale yellow rhombic crystals upon slow evaporation of an aqueous solution at 20–25 °C. These crystals were rapidly decomposed on X-ray irradiation but we were able to determine the crystal lattice parameters: triclinic, $a = 6.61$, $b = 7.57$, $c = 10.69$ Å, $\alpha = 100.47$, $\beta = 104.07$, $\gamma = 99.91°$. In addition, twinned and also very unstable crystals (monoclinic, $a = 20.08$, $b = 6.49$, $c = 20.35$ Å, $\beta = 112.6°$) were picked out from the material obtained after evaporation of the water solution of [$RhCl_2${NH=C(Me)ON=CMe_2}$_2$]Cl. Metathetical reaction of [$RhCl_2${NH=C(Me)ON=CMe_2}$_2$]Cl and Na[SbF_6] in water led to isolation of [$RhCl_2$-{NH=C(Me)ON=CMe_2}$_2$][SbF_6] **3**. Found: C, 19.47; H, 3.34; N, 8.85. $C_{10}H_{20}Cl_2F_6N_4O_2RhSb$ requires C, 18.83; H, 3.16; N, 8.78%. mp = 227 °C (decomp.). FAB$^+$-MS: *m*/*z* 401, [$RhCl_2$-{NH=C(Me)ON=CMe_2}$_2$]$^+$. IR spectrum, cm^{-1} (selected bands): 1681s and 1638s-m *ν*(C=N), 1188m *ν*(C–O) and 658vs *ν*(Sb–F). ^1H NMR in acetone-d_6: *δ* 2.62 (s, 3H), 2.67 (s, 3H), 2.82 (s, 3H) and 10.09 (s, broad, 1H, HN=C). ^{13}C-{^1H} NMR in acetone-d_6: *δ* 15.4 ($1CH_3$), 22.1 ($1CH_3$), 25.0 ($1CH_3$), 173.3 (C=N) and 182.2 (C=N).

Conversion of [$RhCl_3${NH=C(Me)ON=CMe_2}(HON=CMe_2)] into [$RhCl_2${NH=C(Me)ON=CMe_2}$_2$]Cl. Acetonitrile (3 mL) was added to [$RhCl_3${NH=C(Me)ON=CMe_2}(HON=CMe_2)] (0.05 g) and refluxed for 1 h. The starting orange powder was dissolved giving an orange solution from which a yellow crystalline precipitate was released. The reaction mixture was kept at room temperature for 12 h, the precipitate collected on a filter, washed with three 3 mL portions of hot (60 °C) acetonitrile and dried in air 20–25 °C. The crude product was recrystallized from ethanol (2 mL) to form an analytically pure sample. Yield of [$RhCl_2${NH=C(Me)ON=CMe_2}$_2$]Cl 0.04 g, 72%.

Formation of the iminoacylated chelated ligands in the reaction between *mer*-[$RhCl_3(Me_2C{=}NOH)_3$] and MeCN. The complex *mer*-[$RhCl_3(Me_2C{=}NOH)_3$] (0.20 g, 0.47 mmol) was dissolved in acetonitrile (5 mL) and the mixture was heated at 70 °C for 3 min, cooled to room temperature and then left to stand for 1 d at 20–25 °C. The crystalline precipitate was filtered off, washed with three 3 mL portions of acetonitrile and three 3 mL portions of diethyl ether and dried in air at room temperature. Yield of [$RhCl_3${NH=C(Me)ON=CMe_2}(HON=CMe_2)] 0.060 g, 30%. If the reaction mixture is heated at 70 °C for 1.5 h, cooled to room temperature and then left to stand for 3 d at 20–25 °C, the crystalline precipitate that is filtered off,

Table 3 Crystal data and structure refinement for $[RhCl_2\{NH{=}C(Me)ON{=}CMe_2\}_2][SbF_6]$ **3** and $[RhCl_2\{NH{=}C(Me)ONH_2\}_2]Cl$ **5**

	3	**5**
Empirical formula	$C_{10}H_{20}Cl_2F_6N_4O_2RhSb$	$C_4H_{12}Cl_3N_4O_2Rh$
Formula weight	637.87	357.43
T/K	293(2)	293(2)
Crystal system, space group	Monoclinic, $P2_1/c$ (no. 14)	Triclinic, $P\bar{1}$ (no. 2)
a/Å	12.293(2)	8.483(2)
b/Å	10.021(2)	8.508(2)
c/Å	8.811(2)	8.617(2)
α/°		87.86(3)
β/°	106.75(3)	79.59(3)
γ/°		80.42(3)
V/Å^3	1039.4(4)	603.1(3)
Z	2	2
D_c/Mg m^{-3}	2.038	1.968
μ/mm^{-1}	2.414 (Mo-Kα)	1.076 (Ag-Kα)
Reflections collected/unique	1138/1065	2027/1894
Final $R1$, $wR2$ [$I > 2\sigma(I)$]	0.0439, 0.1098	0.0276, 0.0780
all data	0.0439, 0.1098	0.0276, 0.0780

washed with three 3 mL portions of acetonitrile and three 3 mL portions of diethyl ether and dried in air at room temperature is the bis-chelated complex $[RhCl_2\{NH{=}C(Me)ON{=}CMe_2\}_2]Cl$ (0.11 g, 54%).

Hydrolysis of NH=C(Me)ON=CMe$_2$ to give iminoacylated hydroxylamine species. *(i) Isolation of monohydrolysed product.* The complex $[RhCl_2\{NH{=}C(Me)ON{=}CMe_2\}_2]Cl$ (25 mg) was dissolved in 0.1 M HCl (1.5 mL) and the reaction mixture heated at 80 °C for 36 h, whereafter the solvent was rapidly (*ca.* 60 min) evaporated in vacuum at 40 °C and the residue washed with a 0.5 mL portion of acetone and a 0.5 mL portion of diethyl ether. Yield of $[RhCl_2\{NH{=}C(Me)ON{=}CMe_2\}\{NH{=}C(Me)ONH_2\}]Cl{\cdot}H_2O$ **4** 18.5 mg, 81%. Found: C, 18.86; H, 4.32; N, 13.24%. $C_7H_{18}Cl_3N_4O_3Rh$ requires C, 20.23; H, 4.37; N, 13.48%. mp = 144 °C (decomp.). FAB$^+$-MS: *m*/*z* 361, $[M_{cation}]^+$; 325, $[M_{cation} - HCl]^+$. IR spectrum, cm^{-1} (selected bands): 3420vs (br) ν(O–H), 1680 (sh), 1668s and 1642m ν(C=N), 1193s ν(C–O). ^{1}H NMR in D_2O: δ 2.45 (s, 3H, HN=C(*Me*) of the hydrolysed ligand), 2.53 (s, 3H, HN=C(*Me*) of the non-hydrolysed ligand), 2.60 and 2.74 (two s, 3H each, N=C(*Me*)$_2$). ^{13}C-{^{1}H} NMR in D_2O: δ 14.7 (HN=C(*Me*) of the hydrolysed ligand), 14.9 (HN=C(*Me*) of the non-hydrolysed ligand), 20.9 and 24.3 (N=C(Me)$_2$), 172.1 (HN=*C*(Me) of the non-hydrolysed ligand), 176.3 (HN=*C*(Me) of the hydrolysed ligand) and 180.7 (N=*C*(Me)$_2$).

(ii) Isolation of bis-hydrolysed product. The complex *mer*-$[RhCl_3(Me_2C{=}NOH)_3]$ (0.20 g, 0.47 mmol) was dissolved in acetonitrile (5 mL) and the mixture heated at 70 °C for 1.5 h whereafter the solvent was evaporated to dryness at 20–25 °C for about 35 h and then water (5 mL) added to a residue containing a mixture of oil and some crystals. The solution thus obtained was filtered off from a small amount of insoluble material and evaporated to dryness in an open beaker at room temperature for 5 d. The oily residue formed was crystallized on careful washing and stirring with a glass stick, with three 5 mL portions of ethanol. A yellow precipitate thus formed was filtered off with the last portion of ethanol, washed on a filter with three 3 mL portions of EtOH, three 3 mL portions of Et_2O and dried in air at room temperature. Yield of $[RhCl_2\{NH{=}C(Me)ONH_2\}_2]Cl$ **5** 0.04 g, 24%. Found: C, 13.5; H, 3.3; N, 15.4%. $C_4H_{12}Cl_3N_4O_2Rh$ requires C, 13.44; H, 3.38; N, 15.68%. mp = 220 °C (decomp.). FAB$^+$-MS: *m*/*z* 321, $[RhCl_2\{NH{=}C(Me)ONH_2\}_2]^+$. IR spectrum, cm^{-1} (selected bands): 3086 and 3004vs (br) ν(N–H), 1676s ν(C=N) and 1182s-m ν(C–O). ^{1}H NMR spectrum in D_2O: δ 2.40 (s). ^{13}C-{^{1}H} NMR spectrum in D_2O: δ 15.2 (CH_3) and 175.4 (C=N).

Condensation of $[RhCl_2\{NH{=}C(Me)ONH_2\}_2]Cl$ and acetone. The complex $[RhCl_2\{NH{=}C(Me)ONH_2\}_2]Cl$ (0.03 g) was refluxed in a mixture of acetone (1 mL) and ethanol (2 mL) for 20 h. The starting yellow powdered material was dissolved after *ca.* 10 h giving a yellow solution. The reaction mixture was filtered off from a small amount of undissolved material and left to evaporate for 30 h at room temperature. An oily residue formed was crystallized on addition (followed by decanting) of three 1 mL portions of acetone and on continuous stirring with a glass stick. A yellow precipitate thus formed was filtered off with the last portion of acetone, washed on a filter with two 1 mL portions of Me_2CO and dried in air at room temperature. Yield of mixture of $[RhCl_2\{NH{=}C(Me)ON{=}CMe_2\}_2]Cl$ and $[RhCl_2\{NH{=}C(Me)ON{=}CMe_2\}\{NH{=}C(Me)ONH_2\}]Cl{\cdot}H_2O$ 0.01 g.

Structure determination of $[RhCl_2\{NH{=}C(Me)ON{=}CMe_2\}_2][SbF_6]$ 3 and $[RhCl_2\{NH{=}C(Me)ONH_2\}_2]Cl$ 5

Yellow prisms of complex **3** were obtained by recrystallization from an acetonitrile–toluene mixture, while yellow cubes of **5** were grown by slow evaporation of an aqueous solution. Diffraction data were collected on an Enraf-Nonius CAD 4 diffractometer. Data processing was performed with the program PROFIT.[26] The structures were solved by standard Patterson methods (SHELXTL package[27]) and refined by full-matrix least squares based on F^2 using SHELXL 97.[28] The H atoms were located in a Fourier difference map and refined isotropically. Extinction, Lorentz, polarization and absorption corrections were made.[29] Scattering factors from ref. 30. Crystal data are given in Table 3.

CCDC reference number 186/1912.

See http://www.rsc.org/suppdata/dt/b0/b001384f/ for crystallographic files in .cif format.

Acknowledgements

V. Yu. K. and M. A. Z. are very much obliged to INTAS (International Association for the Promotion of Co-operation with Scientists from the New Independent States of the former Soviet Union, grant 97-0166) and the PRAXIS XXI program (grant BCC16428/98) for financial support of this study. G. W. is grateful to the PRAXIS XXI program for a fellowship (BPD11779/97). A. J. L. P. thanks the FCT (Foundation for Science and Technology) and the PRAXIS XXI program for financial support.

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