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Rhodium(III)-mediated oxime–nitrile coupling giving chelated iminoacylated species †

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Treatment of the acetonitrile complex *mer*-$[RhCl_3(MeCN)_3]$ with cyclopentanone oxime $(C_4H_8)C{=}NOH$ resulted in the formation of two rhodium(III) products that contain newly formed chelated iminoacyl ligands, *i.e.* $[RhCl_3\{NH{=}C(Me)ON{=}C(C_4H_8)\}\{HON{=}C(C_4H_8)\}]$ and $[RhCl_2\{NH{=}C(Me)ON{=}C(C_4H_8)\}_2]Cl{\cdot}1.5H_2O$. Only one iminoacylated product, *i.e.* the rhodium(III) complex $[RhCl_2\{NH{=}C(Ph)ON{=}C(C_4H_8)\}_2]Cl{\cdot}H_2O{\cdot}EtOH$, has been isolated in the reaction between the oxime and the benzonitrile complex *mer*-$[RhCl_3(PhCN)_3]$ in ethanol. A *formally* reverse reaction between $[RhCl_3\{HON{=}C(C_4H_8)\}_3]$, prepared on treatment of $RhCl_3{\cdot}4H_2O$ with the oxime in EtOH, and free organonitrile has also been carried out. All products were characterized by elemental analyses (C, H, N, Cl, Rh), FAB^+-MS, IR, ^1H and ^{13}C-$\{^1H\}$ NMR spectroscopies. X-Ray single-crystal analyses were performed for $[RhCl_3\{NH{=}C(Me)ON{=}C(C_4H_8)\}\{HON{=}C(C_4H_8)\}]$, $[RhCl_2\{NH{=}C(Me)ON{=}C(C_4H_8)\}_2]Cl{\cdot}1.5H_2O$, $[RhCl_2\{NH{=}C(Ph)ON{=}C(C_4H_8)\}_2]Cl{\cdot}H_2O{\cdot}2EtOH$ and *mer*-$[RhCl_3\{HON{=}C(C_4H_8)\}_3]$.

Introduction

The synthetic utility of organonitrile metal complexes for preparation of a great variety of new rather exotic compounds by the addition of nucleophiles, such as water–hydroxide, amines with sp^3- and sp^2-nitrogens or mercaptans, to the electrophilically activated carbon atom of the nitrile group has recently been reviewed thoroughly by Michelin *et al.*[4] Recent developments on metal-bound organonitriles include additions of 1,2-bis(diphenylphosphino)ethane to acetonitrile in $[Mo_2(MeCN)_8(ax\text{-}MeCN)][BF_4]_4$,[5] formation of amidrazone complexes on addition of hydrazines,[6] and also our findings of the addition to nitriles co-ordinated to a Rh–Rh unit to give a novel type of metallacycle,[7] addition of ethylenediamine to $[PtCl_2(PhCN)_2]$ to afford $[Pt(NH{=}C(Ph)NHCH_2CH_2NH_2)_2]^{2+}$, a complex that contains two unusual seven-membered organic metallacycles bound to the same platinum(II) center,[8] and the addition of nucleophiles with concerted cyclization of cyanoguanidine that yielded a novel type of azametallacycles, *cis*-$[Pt(PPh_3)_2\{NHC(Nuc){=}NC(NH_2){=}NH\}][BPh_4]$, from reaction of the cyanoguanidine complex *cis*-$[Pt\{NCNC(NH_2)_2\}(PPh_3)_2][BPh_4]_2$ with the appropriate protic nucleophiles (HNuc = alcohols, amines, hydroxylamine or oximes).[9]

Our interest in nucleophilic additions to co-ordinated organonitriles was recently sparked by observation of the facile high-yield reaction between the platinum(IV) complexes $[PtCl_4(RCN)_2]$ and oximes, $R^1R^2C{=}NOH$ ($R^1 = R^2 = Me$; $R^1R^2 = C_4H_8$, C_5H_{10}, (H)Ph, or $(H)C_6H_4(OH)$-*o*), which led to isolation of unusual iminoacylated compounds $[PtCl_4(NH{=}C(R)ON{=}CR^1R^2)_2]$.[1] Owing to the success of that reaction, our further research was first concentrated on the development of an analogous process for $[PtCl_4(RCN)_2]$ and alkylated hydroxylamines[2] and then extended to one-end addition of *vic*-dioximes to the same platinum(IV) precursors to generate platinum(IV)-based metallaligands.[3] We report herein on the extension, to another metal, of the work on addition of oximes, which involves rhodium(III)-mediated addition of $(C_4H_8)C{=}NOH$ to organonitriles giving, in contrast to the previous results,[1–3] a *chelated* iminoacylated species.

† Iminoacylation. Part 4.[1–3]

Experimental

Materials and instrumentation

Cyclopentanone oxime (Aldrich), $RhCl_3{\cdot}4H_2O$ (Reakhim) and solvents were obtained from commercial sources and used as received. The nitrile-based complexes of rhodium(III), *e.g.* $[RhCl_3(MeCN)_3]$[10] and $[RhCl_3(PhCN)_3]$,[11] were prepared in accord with the published methods. The C, H and N elemental analyses were carried out by Microanalytical Services of the Instituto Superior Técnico and St. Petersburg Technological Institute, while Cl and Rh were analysed by the authors. 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 matrices of samples with 8 keV (*ca.* 1.28×10^{15} J) Xe atoms. Mass calibration for the data acquisition system 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.

Formation of iminoacylated chelated ligands in reactions between *mer*-$[RhCl_3(RCN)_3]$ (R = Me or Ph) and $(C_4H_8)C{=}NOH$

***(i) mer*-$[RhCl_3(MeCN)_3]$ generated *in situ*, in water–acetonitrile.** Acetonitrile (2 mL) was added to a solution of $RhCl_3{\cdot}4H_2O$ (0.20 g, 0.71 mmol) in water (3 mL), heated at 65 °C for 20 min until the solution turned dark orange, whereafter $(C_4H_8)C{=}NOH$ (0.16 g, 1.62 mmol) was added. The reaction mixture was then heated for 30 min until the solution became pale yellow, filtered from a small amount of undissolved material on a filter paper and left for 18 h at 20–25 °C. Crystals of $[RhCl_3\{NH{=}C(Me)ON{=}C(C_4H_8)\}\{HON{=}C(C_4H_8)\}]$ **2** were filtered off, washed with three 3 mL portions

of water, three 3 mL portions of ethanol and three 3 mL portions of diethyl ether and dried in air at room temperature. Yield 0.03 g (9%).

The filtrate was placed in an open beaker and left in air at room temperature. After evaporation of *ca*. 2/3 of its volume, crystals of $[RhCl_2\{NH{=}C(Me)ON{=}C(C_4H_8)\}_2]Cl{\cdot}1.5H_2O$ **3** were collected on a filter, washed with three 3 mL portions of acetonitrile, three 3 mL portions of diethyl ether and dried in air. Yield 0.02 g (5%). The new filtrate was evaporated to dryness at room temperature, the residue dissolved in acetonitrile (3 mL) and then a second fraction (0.12 g, 30%) of the less pure complex isolated upon addition of diethyl ether (20 mL). The reaction can also be carried out similarly starting from *mer*-$[RhCl_3(MeCN)_3]$ but yields are lower.

$[RhCl_3\{NH{=}C(Me)ON{=}C(C_4H_8)\}\{HON{=}C(C_4H_8)\}]$ (Found: C, 32.1; H, 4.6; Cl, 24.1; N, 9.5; Rh, 22.7. $C_{12}H_{21}Cl_3N_3O_2Rh$ requires C, 32.1; H, 4.7; Cl, 23.7; N, 9.4; Rh, 22.9%): mp = 185 °C; FAB$^+$-MS *m/z* 412, $[M - Cl]^+$; 376, $[M - 2Cl - H]^+$. Poor solubility of this compound precludes recording the ^{1}H NMR spectrum at room temperature: ^{1}H NMR ($CDCl_3$, 50 °C): δ 1.83 (m, 4 H), 2.00 (m, 4 H), 2.56 (s, 3 H, Me), 2.98 (s, br, 2 H), 3.12 (s, br, 2 H), 3.30 (s, br, 4 H), 8.55 (s, br, 1 H) and 9.97 (s, sharp, 1 H). Poor solubility precludes recording the ^{13}C-{^{1}H} NMR spectrum in reasonable accumulation time. IR, cm^{-1} (selected bands): 1630m, ν(C=N); 1161, ν(C–O).

$[RhCl_2\{NH{=}C(Me)ON{=}C(C_4H_8)\}_2]Cl{\cdot}1.5H_2O$ (Found: C, 32.6; H, 5.1; Cl, 21.6; N, 11.2; Rh, 19.7. $C_{14}H_{24}Cl_3N_4O_2Rh{\cdot}1.5H_2O$ requires C, 32.6; H, 5.3; Cl, 20.6; N, 10.8; Rh, 19.9%): mp = 186 °C (decomp.); FAB$^+$-MS *m/z* 453, $[RhCl_2\{NH{=}C(Me)ON{=}C(C_4H_8)\}_2]^+$; ^{1}H NMR ($CD_3OD$) δ 2.05 (m, 4 H, CH_2), 2.56 (s, 3 H, CH_3), 3.22 (t, 7.5 Hz, 2 H, CH_2), 3.31 (t, 7.5 Hz, 2 H, CH_2), NH was not detected; ^{13}C-{^{1}H} NMR (CD_3OD) δ 14.7 (CH_3), 25.8, 26.4, 35.7, 35.9 ((CH_2)$_4$), 173.5 and 186.0 (C=N); IR, cm^{-1} (selected bands) 1645m and 1682m, ν(C=N); 1183, ν(C–O).

***(ii) mer*-[RhCl$_3$(PhCN)$_3$] in EtOH.** The complex *mer*-$[RhCl_3(PhCN)_3]$ (0.20 g, 0.39 mmol) was dissolved in hot (*ca*. 60 °C) ethanol (5 mL), and 0.080 g (0.81 mmol) of cyclopentanone oxime was added. When the reaction mixture was immediately cooled to 20–25 °C, the beginning of crystallization was observed after 30 min. The crystals were separated by filtration after 20 h. Yield of *mer*-$[RhCl_3\{HON{=}C(C_4H_8)\}_3]$ 0.03 g, 15%. When the reaction mixture was heated at 60 °C for 4 h, evaporated to 2 mL and then left to stand for one week at room temperature, pale yellow crystals were obtained, collected on a filter, washed with ethanol (three 3 mL portions), chloroform (three 3 mL portions) and diethyl ether (three 3 mL portions) and dried in air at room temperature. Yield of $[RhCl_2\{NH{=}C(Ph)ON{=}C(C_4H_8)\}_2]Cl{\cdot}H_2O{\cdot}2EtOH$ **4** 0.04 g (14%).

$[RhCl_2\{NH{=}C(Ph)ON{=}C(C_4H_8)\}_2]Cl{\cdot}H_2O{\cdot}2EtOH$ (Found: C, 43.8; H, 4.7; Cl, 16.2; N, 7.9; Rh, 15.2. $C_{28}H_{42}Cl_3N_4O_5Rh$ requires C, 46.5; H, 5.9; Cl, 14.7; N, 7.7; Rh, 14.2%): mp = 155 °C (decomp.); FAB$^+$-MS *m/z* 577 $[RhCl_2\{NH{=}C(Ph)ON{=}C(C_4H_8)\}_2]^+$; ^{1}H NMR (DMSO-$d_6$–methanol-$d_4$ (1 : 1, v/v), δ 2.11 (m, 4 H), 3.50 (t, 6.8, 2 H) and 3.62 (t, 6.8, 2 H)-(C_4H_8), 7.71 (t, 7.5, 2 H), 7.85 (t, 7.0 1 H) and 8.10 (d, 8.2 Hz, 2 H) (Ph); ^{13}C-{^{1}H} NMR (DMSO-d_6–methanol-d_4 (1 : 1, v/v)). δ 25.4, 26.1, 35.0, 35.5 ({CH_2}$_4$), 127.3, 133.6, 134.2, 139.7 (Ph), 173.6 and 187.4 (C=N); IR, cm^{-1} (selected bands) 3512m, (br) and 3408m (br), ν(O–H); 1632vs, ν(C=N); 695 m-s, δ(C–H).

Formation of iminoacylated chelated ligands in reactions between *mer*-[RhCl$_3${HON=C(C$_4$H$_8$)}$_3$] and the nitriles RCN (R = Me or Ph)

(i) MeCN in MeCN–EtOH. The complex *mer*-$[RhCl_3\{HON{=}C(C_4H_8)\}_3]$ (0.20 g, 0.39 mmol) was dissolved in acetonitrile (5 mL) on boiling, ethanol (2 mL) added dropwise and the mixture heated at 65 °C for 30 min then cooled to room temperature. An oily residue, that also contained some solid material, obtained after evaporation of the solvent at room temperature (*ca.* 2 d) was dissolved in acetonitrile (3 mL) and left to stand for 6 h. Crystals were filtered off, washed with two 3 mL portions of MeCN and two 3 mL portions of $CHCl_3$ and dried in air at 20–25 °C. Yield of $[RhCl_2\{NH{=}C(Me)ON{=}C(C_4H_8)\}_2]Cl{\cdot}1.5H_2O$ 0.04 g, 20%.

(ii) PhCN. All our attempts to cause the complex and benzonitrile to react in both chloroform and neat PhCN failed. In each case a mixture of brownish oily unidentified products was obtained.

Synthesis of *mer*-[RhCl$_3${HON=C(C$_4$H$_8$)}$_3$] 1

The oxime (1.24 mmol) was added at 20–25 °C to a solution of $RhCl_3{\cdot}4H_2O$ (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 dark orange, then cooled to room temperature. A crystalline yellow precipitate was formed 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 *ca*. 50% (Found: C, 36.3; H, 5.3; Cl, 21.1; N, 8.3; Rh, 20.5. $C_{15}H_{27}Cl_3N_3O_3Rh$ requires C, 35.6; H, 5.4; Cl, 21.0; N, 8.3; Rh, 20.3%). FAB$^+$-MS: *m/z* 470, $[M - Cl]^+$; 434, $[M - 2Cl - H]^+$; and 398, $[M - 3Cl - 2H]^+$. mp = 200 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ 1.82 (m, 12 H), 2.94 (m, 8 H), 3.02 (m, 4 H), 9.37 (s, br, 2 H) and 9.58 (s, br, 1 H). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ 23.9 ($3CH_2$), 25.7 ($2CH_2$), 25.8 ($1CH_2$), 33.4 ($1CH_2$), 33.5 ($2CH_2$), 34.0 ($2CH_2$), 34.2 ($1CH_2$), 184.4 (2C=N) and 184.9 (1C=N). IR spectrum, cm^{-1} (selected bands): 1620m, ν(C=N); 1280, δ(OH).

Crystal structure determinations of complexes 1–4

Dark orange prisms of complexes **1** and **2** were obtained directly from the reaction mixture, crystals of **3** and **4** on slow evaporation of aqueous solutions. Diffraction data were collected on Syntex P2$_1$ (**1**) (Mo-Kα radiation, graphite monochromator, ω method), Enraf-Nonius CAD 4 (**2**, **4**) and Syntex P-1 (**3**) (Mo-Kα radiation, β-filter) diffractometers. Standard reflections were measured every 60 min [every 50 reflections for **1**] and showed practically no change with time (±1%). Diffractometer data were processed by the program PROFIT [12] with profile analysis of reflections. The structures were solved by means of Fourier syntheses based upon the Rh atom coordinates obtained from the Patterson synthesis using the SHELXTL package.[13] After that all reflections with $I \leq 2\sigma(I)$ [$I < 3\sigma(I)$ for **1**] were excluded from calculations. Refinement was done by full-matrix least squares based on F^2 using the SHELXL 97 package.[14] All non-H atoms were treated anisotropically. Extinction and Lorentz-polarization corrections were applied, and absorption correction for **1** and **4**.[15] Scattering factors were from ref. 16. Crystal data are given in Table 1, bond distances and angles in Tables 2–5.

CCDC reference number 186/1557.

See http://www.rsc.org/suppdata/dt/1999/3047/ for crystallographic files in .cif format.

Results and discussion

It is generally believed that additions to organonitriles proceed *via* nucleophilic attack at the carbon atom of the C≡N group.[4,17] In accord with these views, these reactions should, in principle, be facilitated by application of organonitrile complexes with the metal ion in a high oxidation state, introducing acceptor groups R to RC≡N, increasing the overall positive charge on

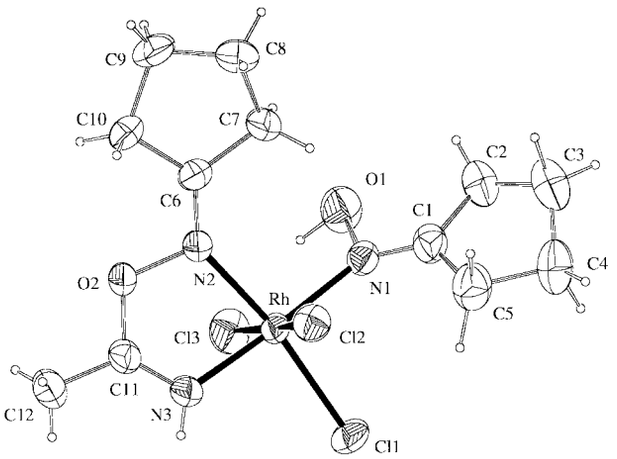


Fig. 1 An ORTEP[21] drawing of $[RhCl_3\{NH{=}C(Me)ON{=}C(C_4H_8)\}\{HON{=}C(C_4H_8)\}]$ **2** with the atomic numbering scheme.

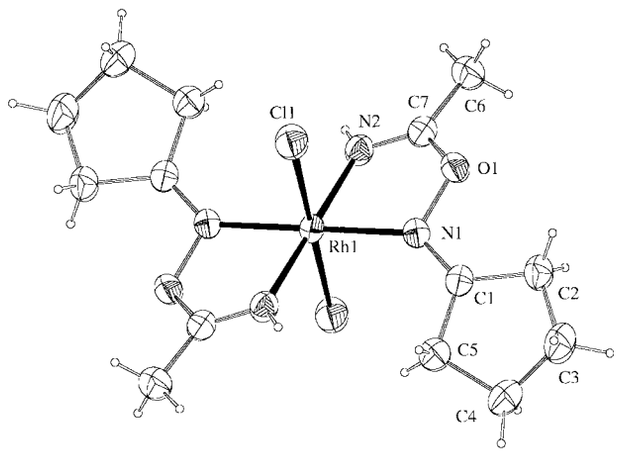
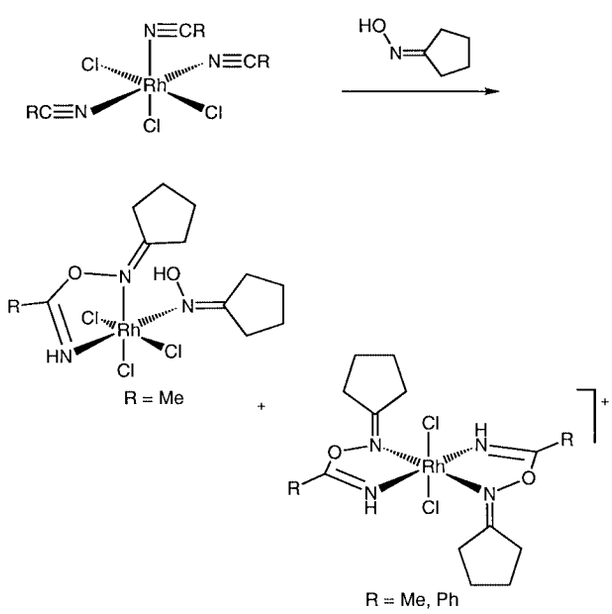


Fig. 2 An ORTEP drawing of $[RhCl_2\{NH{=}C(Me)ON{=}C(C_4H_8)\}_2]^+$ **3** with the atomic numbering scheme.

a complex ion and the use of supporting ligands with good π-acceptor properties. The main objective of the present study was to determine whether the results obtained for the platinum(IV) nitrile complexes and oximes (see above) were peculiar to that system, or whether the reactions are characteristic of other metal complexes where *the central ion is in a high oxidation state*. The logical candidates for investigation were the organonitrile complexes of rhodium(III) with their well developed substitution chemistry and a number of previously reported crystal structures.[10,18] For this study we addressed the complexes *mer*-$[RhCl_3(RCN)_3]$ (R = Me[10] or Ph[11]) and investigated their reactions with cyclopentanone oxime that is one of the simplest ketoximes frequently used for reactivity studies.[19,20]

When the acetonitrile complex *mer*-$[RhCl_3(MeCN)_3]$, prepared *in situ* from $RhCl_3{\cdot}4H_2O$ and MeCN in water, was treated with $(C_4H_8)C{=}NOH$ two products were isolated as solids, *i.e.* $[RhCl_3\{NH{=}C(Me)ON{=}C(C_4H_8)\}\{HON{=}C(C_4H_8)\}]$ **2** (yield is *ca.* 10%) and $[RhCl_2\{NH{=}C(Me)ON{=}C(C_4H_8)\}_2]Cl{\cdot}1.5H_2O$ **3** (yield is *ca.* 40%) (Scheme 1). Both compounds were characterized by single-crystal X-ray diffraction analysis (Figs. 1 and 2).



Scheme 1

The structure of the first product, **2** consists of an octahedrally co-ordinated rhodium(III) center in which two adjacent positions are filled with the newly formed iminoacylated ligand, three *mer* positions with Cl^- ligands and one site with cyclopentanone oxime (Fig. 1). Geometrical parameters of the co-ordinated cyclopentanone oxime agree well with those of *mer*-$[RhCl_3\{HON{=}C(C_4H_8)\}_3]$ (see below). The Rh–N(3) bond length is normal, while Rh–N(2) [2.025(3) Å] and Rh–N(1) [2.066(3) Å] are slightly larger than those observed for many other *vic*-dioxime/dioximato complexes of rhodium(III) [1.97–2.00 Å].[22] The Rh–Cl bond lengths [2.316–2.351 Å] are normal.[10,23,24] In the iminoacylated ligand the N–O bond [1.456(3) Å] is longer than the N(1)–O(1) one [1.424(4) Å] in the neighbouring cyclopentanone oxime. The two C=N bonds are equal within 3σ and both distances coherent with reported values.[25]

The structure of the second product **3** comprises two crystallographically independent molecules of $[RhCl_2\{NH{=}C(Me)ON{=}C(C_4H_8)\}_2]Cl{\cdot}1.5H_2O$. In both the co-ordination polyhedron of $[RhCl_2\{NH{=}C(Me)ON{=}C(C_4H_8)\}_2]^+$ is a slightly distorted octahedron and the rhodium atom is at the center of symmetry. The two iminoacyl ligands are mutually *trans* and bound to the rhodium(III) centre through nitrogens. The Rh–N distances [average 2.018 Å] are slightly larger than those observed in other monocationic complexes of rhodium(III) that contain *vic*-dioxime/dioximato ligands [1.94–2.00 Å] but the Rh–Cl bonds [average 2.334 Å] correspond well to reported data for rhodium(III) complexes $[RhCl_2(Hdmg)]$[23] [average 2.34 Å] and [dichloro(ethanedial dioxime)(ethanedial dioximato)-rhodium [average 2.33 Å[24]], although they have different overall charges. Within the iminoacyl ligands the two different C=N bonds are almost identical and the observed distances correspond to mean values of C=N double bonds.[25] It is noticeable that bidentate co-ordination of the iminoacyl species does not affect either the C=N or the N–O distances as compared to *trans*-$[PtCl_4(NH{=}C(Me)ON{=}CR^1R^2)_2]$ where these species are monodentate ligands.

From the reaction between the benzonitrile complex *mer*-$[RhCl_3(PhCN)_3]$ and cyclopentanone oxime in ethanol (solvent chosen on account of the solubility of the starting materials) we isolated, in a moderate yield, only one iminoacylated product, *i.e.* the rhodium(III) complex $[RhCl_2\{NH{=}C(Ph)ON{=}C(C_4H_8)\}_2]Cl$ **4** (Fig. 3). The latter crystallizes from the reaction mixture as the monoaqua bis(ethanol) solvate as was verified by the X-ray diffraction study. The principal features of the structure are very similar to those observed in $[RhCl_2\{NH{=}C(Me)ON{=}C(C_4H_8)\}_2]^+$. In $[RhCl_2\{NH{=}C(Ph)ON{=}C(C_4H_8)\}_2]Cl{\cdot}H_2O{\cdot}2EtOH$ the chloride counter ion and the H_2O molecule are in statistically occupied positions and the ethanol molecules are also disordered in two positions (atoms C(2EA) and C(2EB)). FAB mass spectrometry, IR and ^1H NMR data give strong evidence in favour of the formation of the $[RhCl_2\{NH{=}C(Ph)ON{=}C(C_4H_8)\}_2]^+$ cation. However, typical elemental analyses presented in the Experimental section are not satisfactory probably due to additional water molecules present in the

Table 1 Crystal data and structure refinement for complexes **1**–**4**

	1	**2**	**3**	**4**
Formula	$C_{15}H_{27}Cl_3N_3O_3Rh$	$C_{12}H_{21}Cl_3N_3O_2Rh$	$C_{14}H_{27}Cl_3N_4O_{3.5}Rh$	$C_{28}H_{42}Cl_3N_4O_5Rh$
M	506.6	448.58	516.66	723.93
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a/Å	11.640(6)	11.512(2)	8.524(2)	8.866(2)
b/Å	8.898(5)	9.724(2)	11.529(2)	10.358(2)
c/Å	19.75(8)	15.694(3)	12.116(2)	10.952(2)
α/°			67.21(3)	109.58(3)
β/°	98.03	107.06(3)	94.35(3)	97.65(3)
γ/°			82.12(3)	112.09(3)
V/Å^3	2025(8)	1679.5(6)	1076.5(4)	838.5(5)
Z	4	4	2	1
T/K	293(2)	293(2)	293(2)	293(2)
D_c/g cm^{-3}	1.651	1.774	1.594	1.434
Independent reflections	1558	1982	3094	1618
R_{int}	0.094	0.014	0.0	0.012
Parameters	226	270	343	241
Goodness of fit on F^2	1.019	1.111	1.045	1.079
*R*1, *wR*2 [$I > 2\sigma(I)$]	0.0450, 0.1075	0.0211, 0.0559	0.0316, 0.0824	0.0332, 0.0907

Table 2 Bond lengths (Å) and angles (°) for [$RhCl_3${NH=C(Me)ON=C(C_4H_8)}{HON=C(C_4H_8)}] **2**

Rh–N(3)	1.977(3)	N(3)–C(11)	1.261(5)
Rh–N(2)	2.025(3)	C(1)–C(2)	1.495(6)
Rh–N(1)	2.066(3)	C(1)–C(5)	1.504(6)
Rh–Cl(1)	2.3160(9)	C(2)–C(3)	1.529(6)
Rh–Cl(2)	2.3337(10)	C(3)–C(4)	1.505(8)
Rh–Cl(3)	2.3513(11)	C(4)–C(5)	1.535(6)
O(1)–N(1)	1.424(4)	C(6)–C(10)	1.495(5)
O(2)–C(11)	1.345(4)	C(6)–C(7)	1.494(5)
O(2)–N(2)	1.456(3)	C(7)–C(8)	1.534(6)
N(1)–C(1)	1.258(4)	C(8)–C(9)	1.488(6)
N(2)–C(6)	1.280(4)	C(9)–C(10)	1.522(6)
		C(11)–C(12)	1.481(5)
N(3)–Rh–N(2)	78.61(12)	C(6)–N(2)–Rh	139.6(2)
N(3)–Rh–N(1)	175.70(12)	O(2)–N(2)–Rh	111.06(18)
N(2)–Rh–N(1)	98.79(11)	C(11)–N(3)–Rh	117.2(3)
N(3)–Rh–Cl(1)	91.93(10)	N(1)–C(1)–C(2)	125.7(4)
N(2)–Rh–Cl(1)	170.22(8)	N(1)–C(1)–C(5)	123.9(4)
N(1)–Rh–Cl(1)	90.80(8)	C(2)–C(1)–C(5)	110.4(4)
N(3)–Rh–Cl(2)	89.48(10)	C(1)–C(2)–C(3)	103.4(4)
N(2)–Rh–Cl(2)	86.50(9)	C(4)–C(3)–C(2)	103.4(4)
N(1)–Rh–Cl(2)	93.80(8)	C(3)–C(4)–C(5)	103.2(4)
Cl(1)–Rh–Cl(2)	90.97(4)	C(1)–C(5)–C(4)	101.7(4)
N(3)–Rh–Cl(3)	87.72(10)	N(2)–C(6)–C(10)	125.7(3)
N(2)–Rh–Cl(3)	90.04(9)	N(2)–C(6)–C(7)	122.9(3)
N(1)–Rh–Cl(3)	88.86(9)	C(10)–C(6)–C(7)	111.4(3)
Cl(1)–Rh–Cl(3)	92.08(4)	C(6)–C(7)–C(8)	102.2(3)
Cl(2)–Rh–Cl(3)	175.92(4)	C(9)–C(8)–C(7)	104.7(4)
C(11)–O(2)–N(2)	112.4(2)	C(8)–C(9)–C(10)	105.3(3)
C(1)–N(1)–O(1)	109.9(3)	C(6)–C(10)–C(9)	103.1(3)
C(1)–N(1)–Rh	137.3(3)	N(3)–C(11)–O(2)	119.4(3)
O(1)–N(1)–Rh	112.7(2)	N(3)–C(11)–C(12)	128.6(4)
C(6)–N(2)–O(2)	108.7(3)	O(2)–C(11)–C(12)	111.9(3)

Table 3 Bond lengths (Å) and angles (°) for [$RhCl_2${NH=C(Me)ON=C(C_4H_8)}$_2$]Cl·1.5H_2O **3**

Rh(1)–N(1)	2.013(3)	C(3)–C(4)	1.507(8)
Rh(1)–N(2)	2.031(3)	C(4)–C(5)	1.525(6)
Rh(1)–Cl(1)	2.3368(11)	C(6)–C(7)	1.479(6)
Rh(2)–N(1′)	2.007(3)	O(1′)–C(7′)	1.349(5)
Rh(2)–N(2′)	2.020(3)	O(1′)–N(1′)	1.447(4)
Rh(2)–Cl(2)	2.3299(13)	N(1′)–C(1′)	1.269(5)
O(1)–C(7)	1.358(5)	N(2′)–C(7′)	1.268(5)
O(1)–N(1)	1.442(4)	C(1′)–C(2′)	1.501(6)
N(1)–C(1)	1.276(5)	C(1′)–C(5′)	1.497(7)
N(2)–C(7)	1.269(5)	C(2′)–C(3′)	1.513(10)
C(1)–C(5)	1.491(6)	C(3′)–C(4′)	1.471(12)
C(1)–C(2)	1.497(5)	C(4′)–C(5′)	1.521(8)
C(2)–C(3)	1.521(6)	C(6′)–C(7′)	1.484(6)
N(1)–Rh(1)–N(1^1)	180.0	C(3)–C(4)–C(5)	103.9(4)
N(1)–Rh(1)–N(2)	76.62(12)	C(1)–C(5)–C(4)	103.0(4)
N(2)–Rh(1)–Cl(1^1)	91.47(9)	N(2)–C(7)–O(1)	119.1(3)
N(1)–Rh(1)–Cl(1)	88.60(9)	N(2)–C(7)–C(6)	128.9(4)
Cl(1^1)–Rh(1)–Cl(1)	180.0	O(1)–C(7)–C(6)	112.0(3)
N(1^2)–Rh–(2)–N(2′)	103.03(13)	C(7′)–O(1′)–N(1′)	110.9(3)
N(1′)–Rh(2)–N(2′)	76.97(13)	C(1′)–N(1′)–O(1′)	110.5(3)
N(1′)–Rh(2)–Cl(2)	89.10(10)	C(1′)–N(1′)–Rh(2)	137.0(3)
N(2′)–Rh(2)–Cl(2)	87.85(10)	O(1′)–N(1′)–Rh(2)	111.9(2)
Cl(2^2)–Rh(2)–Cl(2)	180.0	C(7′)–N(2′)–Rh(2)	115.7(3)
C(7)–O(1)–N(1)	110.5(3)	N(1′)–C(1′)–C(2′)	126.7(4)
C(1)–N(1)–O(1)	110.4(3)	N(1′)–C(1′)–C(5′)	122.4(4)
C(1)–N(1)–Rh(1)	136.8(3)	C(2′)–C(1′)–C(5′)	110.7(4)
O(1)–N(1)–Rh(1)	112.61(19)	C(1′)–C(2′)–C(3′)	103.6(5)
C(7)–N(2)–Rh(1)	115.9(3)	C(4′)–C(3′)–C(2′)	107.0(5)
N(1)–C(1)–C(5)	112.5(3)	C(3′)–C(4′)–C(5′)	105.9(7)
N(1)–C(1)–C(2)	126.6(3)	C(1′)–C(5′)–C(4′)	102.0(5)
C(5)–C(1)–C(2)	110.9(3)	N(2′)–C(7′)–O(1′)	119.2(3)
C(1)–C(2)–C(3)	103.4(3)	N(2′)–C(7′)–C(6′)	128.3(4)
C(4)–C(3)–C(2)	105.1(4)	O(1′)–C(7′)–C(6′)	112.6(4)

Symmetry transformations used to generate equivalent atoms: 1 $-x$, $-y$, $-z+1$; 2 $-x$, $-y$, $-z$.

crystal lattice, but they are highly disordered and were not observed in the X-ray diffraction experiment.

We have also carried out a *formally* reverse reaction between a (cyclopentanone oxime)rhodium(III) complex and free organonitrile. For this we prepared the rhodium(III) precursor [$RhCl_3${HON=C(C_4H_8)}$_3$] **1** on treatment of $RhCl_3$·4H_2O with the oxime in ethanol. In **1** three Cl and three N atoms form a slightly distorted octahedral co-ordination around the Rh atom with angles close to 90 and 180° (Fig. 4). The oxime ligands are in *mer* positions and co-ordinated *via* nitrogens. The Rh–N interatomic distances are slightly higher than those observed in rhodium(III) complexes[22–24] with *vic*-dioxime/dioximato ligands. All other bonds and angles are normal. The ^{1}H and ^{13}C-{^{1}H} NMR data both show two signal sets for the oxime moieties in a ratio of 2:1, thus confirming that the meridional structure of the complex persists in solution. It is worthwhile to mention that despite the simplicity of the structure of *mer*-[$RhCl_3${HON=C(C_4H_8)}$_3$] this is the first example of a structurally characterized rhodium(III) complex that contains so-called 'simple'[19,20] oximes. Previous examples include only complexes with *vic*-dioxime/dioximato ligands.[22–24]

Treatment of *mer*-[$RhCl_3${HON=C(C_4H_8)}$_3$] with acetonitrile in ethanol leads to [$RhCl_2${NH=C(Me)ON=C(C_4H_8)}$_2$]Cl·1.5H_2O. It is remarkable that in neat non-dried acetonitrile, *i.e.* without addition of ethanol, the reaction does not proceed at all even on prolonged heating (3 h, 60 °C) and only the starting rhodium material was recovered. The imino-

Table 4 Bond lengths (Å) and angles (°) for $[RhCl_2\{NH{=}C(Ph)ON{=}C(C_4H_8)\}_2]Cl{\cdot}H_2O{\cdot}2EtOH$ **4**

Rh–N(2)	2.006(4)	C(4)–C(5)	1.371(10)
Rh–N(1)	2.014(4)	C(5)–C(6)	1.370(10)
Rh–Cl(1)	2.3337(17)	C(6)–C(7)	1.390(8)
O(1)–C(1)	1.349(6)	C(8)–C(9)	1.494(8)
O(1)–N(2)	1.449(5)	C(8)–C(12)	1.496(8)
N(1)–C(1)	1.274(6)	C(9)–C(10)	1.509(11)
N(2)–C(8)	1.282(7)	C(10)–C(11)	1.487(10)
C(1)–C(2)	1.467(6)	C(11)–C(12)	1.518(10)
C(2)–C(3)	1.384(8)	O(1E)–C(1E)	1.50(2)
C(2)–C(7)	1.384(8)	C(1E)–C(2EA)	1.24(3)
C(3)–C(4)	1.386(7)	C(1E)–C(2EB)	1.28(3)
$N(2^1)$–Rh–N(2)	180.0	C(7)–C(2)–C(1)	119.1(5)
$N(2^1)$–Rh–N(1)	103.25(17)	C(2)–C(3)–C(4)	118.8(6)
N(2)–Rh–N(1)	76.75(17)	C(5)–C(4)–C(3)	121.0(6)
N(2)–Rh–$Cl(1^1)$	91.25(14)	C(6)–C(5)–C(4)	120.3(6)
N(1)–Rh–$Cl(1^1)$	91.26(13)	C(5)–C(6)–C(7)	119.7(7)
$Cl(1^1)$–Rh–Cl(1)	180.0	C(2)–C(7)–C(6)	119.9(6)
C(1)–O(1)–N(2)	110.3(3)	N(2)–C(8)–C(9)	126.3(5)
C(1)–N(1)–Rh	115.8(4)	N(2)–C(8)–C(12)	122.9(5)
C(8)–N(2)–O(1)	110.4(4)	C(9)–C(8)–C(12)	110.7(5)
C(8)–N(2)–Rh	137.5(3)	C(8)–C(9)–C(10)	104.8(6)
O(1)–N(2)–Rh	111.8(3)	C(11)–C(10)–C(9)	106.6(7)
N(1)–C(1)–O(1)	119.0(4)	C(10)–C(11)–C(12)	106.7(6)
N(1)–C(1)–C(2)	127.6(5)	C(8)–C(12)–C(11)	103.0(5)
O(1)–C(1)–C(2)	113.4(4)	C(2EA)–C(1E)–O(1E)	109(2)
C(3)–C(2)–C(7)	120.3(5)	C(2EB)–C(1E)–O(1E)	121(2)
C(3)–C(2)–C(1)	120.6(5)		

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

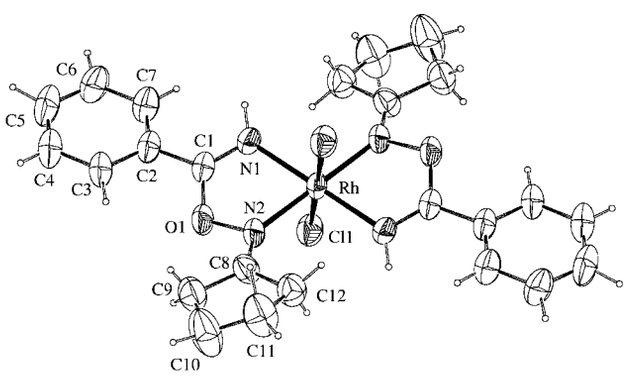


Fig. 3 An ORTEP drawing of $[RhCl_2\{NH{=}C(Ph)ON{=}C(C_4H_8)\}_2]^+$ **4** with the atomic numbering scheme.

acylation of *oxime* rather than *organonitrile* complexes was first reported by Grigg *et al.*[26] and also later by Zerbib *et al.*[27] who observed complicated processes between oxovanadium(IV) aldoxime and ketoxime complexes, for example $[VO\{HON{=}CH(O)C_6H_4\}_2]$, under treatment with acetonitrile. In the course of oxidation of the vanadium(IV), loss of one oxime ligand and addition of MeCN, the *iminoacyl* oxovanadium complex $[VO_2\{NH{=}C(Me)ON{=}CH(O)C_6H_4\}]$ is formed. The oxime–nitrile coupling appears to be promoted by oxidation of the metal to V^V,[26] but our rhodium(III) and platinum(IV) complexes present sufficiently high metal oxidation states to induce the reaction in this way. In general, the observed oxime coupling is metal-mediated. Indeed, as we have shown previously,[1] the addition of oximes to organonitriles does not proceed in the absence of metal complex even under rather harsh reaction conditions.

It is well known that rhodium(III) complexes are much more labile than similar complexes of platinum(IV) and this general relative behaviour is in accord with the extended variety of products we have observed in the reactions of the oxime with *mer*-$[RhCl_3(RCN)_3]$, in comparison with $[PtCl_4(RCN)_2]$, that proceed also with a lower selectivity and with moderate isolated yields. Moreover, the rhodium(III) system brings further features to the oxime–nitrile coupling reaction, in particular by

Table 5 Bond lengths (Å) and angles (°) for *mer*-$[RhCl_3\{HON{=}C(C_4H_8)\}_3]$ **1**

Rh–Cl(1)	2.364(10)	C(2)–C(3)	1.532(16)
Rh–Cl(2)	2.337(10)	C(3)–C(4)	1.502(17)
Rh–Cl(3)	2.358(10)	C(4)–C(5)	1.530(15)
Rh–N(1)	2.053(11)	C(6)–C(7)	1.513(17)
Rh–N(2)	2.056(12)	C(6)–C(10)	1.509(17)
Rh–N(3)	2.062(12)	C(7)–C(8)	1.539(18)
O(1)–N(1)	1.410(12)	C(8)–C(9)	1.474(18)
O(2)–N(2)	1.391(12)	C(9)–C(10)	1.496(17)
O(3)–N(3)	1.421(12)	C(11)–C(12)	1.507(16)
N(1)–C(1)	1.298(13)	C(11)–C(15)	1.506(15)
N(2)–C(6)	1.290(14)	C(12)–C(13)	1.527(17)
N(3)–C(11)	1.280(14)	C(13)–C(14)	1.508(19)
C(1)–C(2)	1.509(15)	C(14)–C(15)	1.516(17)
C(1)–C(5)	1.482(15)		
Cl(1)–Rh–Cl(2)	175.52(11)	C(2)–C(3)–C(4)	105.4(9)
Cl(1)–Rh–Cl(3)	88.18(12)	C(3)–C(4)–C(5)	103.8(8)
Cl(1)–Rh–N(1)	89.8(2)	C(1)–C(5)–C(4)	102.8(8)
Cl(1)–Rh–N(2)	91.6(2)	N(2)–C(6)–C(7)	123.7(9)
Cl(1)–Rh–N(3)	88.2(2)	N(2)–C(6)–C(10)	126.8(9)
Cl(2)–Rh–Cl(3)	87.65(12)	C(7)–C(6)–C(10)	109.5(9)
Cl(2)–Rh–N(1)	94.3(2)	C(6)–C(7)–C(8)	104.4(9)
Cl(2)–Rh–N(2)	90.0(2)	C(7)–C(8)–C(9)	104.6(10)
Cl(2)–Rh–N(3)	90.1(2)	C(8)–C(9)–C(10)	107.8(10)
Cl(3)–Rh–N(1)	117.9(3)	C(6)–C(10)–C(9)	102.4(9)
Cl(3)–Rh–N(2)	88.1(2)	N(3)–C(11)–C(12)	124.8(9)
Cl(3)–Rh–N(3)	89.7(2)	N(3)–C(11)–C(15)	124.6(9)
N(1)–Rh–N(2)	92.6(3)	C(12)–C(11)–C(15)	110.6(8)
N(1)–Rh–N(3)	89.6(3)	C(11)–C(12)–C(13)	103.7(9)
N(2)–Rh–N(3)	177.8(3)	C(12)–C(13)–C(14)	105.1(9)
Rh–N(1)–O(1)	112.4(5)	C(13)–C(14)–C(15)	105.2(10)
Rh–N(1)–C(1)	135.2(7)	C(11)–C(15)–C(14)	102.6(9)
O(1)–N(1)–C(1)	112.4(7)	C(2)–C(1)–C(5)	111.1(8)
Rh–N(2)–O(2)	115.4(6)	C(1)–C(2)–C(3)	102.8(8)
Rh–N(2)–C(6)	132.7(7)	O(3)–N(3)–C(11)	111.4(8)
O(2)–N(2)–C(6)	111.9(8)	N(1)–C(1)–C(2)	122.6(9)
Rh–N(3)–O(3)	113.8(6)	N(1)–C(1)–C(5)	126.3(9)
Rh–N(3)–C(11)	134.9(7)		

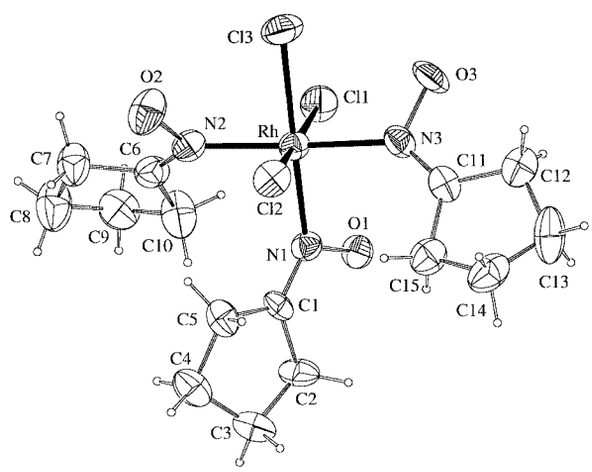


Fig. 4 An ORTEP drawing of *mer*-$[RhCl_3\{(HON{=}C(C_4H_8)\}_3]$ **1** with the atomic numbering scheme.

(*i*) taking advantage of the driving effect of chelation of the iminoacylated product (formation of mono- and di-chelated species) and by (*ii*) promoting the reaction through metal activation of either the nitrile or the oxime ligand thus allowing the iminoacylation to start from either the nitrile or oxime complexes. The synthetic potential of these new aspects probably deserve further exploration.

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