

Facile rhenium(IV)-mediated coupling of acetonitrile and oximes†

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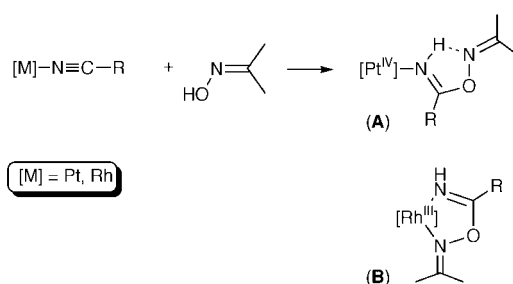
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Addition of oximes RR'C=NOH [R/R' = Me/Me, C₄H₈, C₅H₁₀, C₉H₁₈, C₉H₁₆ or Me/C(Me)NOH] to the acetonitrile ligands in *cis*-[ReCl₄(MeCN)₂] proceeded smoothly at room temperature within a few minutes to give *cis*-[ReCl₄{NH=C(Me)ON=CRR'}₂] in almost quantitative yield. All complexes were characterized by elemental analysis, IR spectroscopy and FAB mass spectrometry. Structure determination, performed for *cis*-[ReCl₄{NH=C(Me)ON=C(C₅H₁₀)₂}]·MeCN and *cis*-[ReCl₄{NH=C(Me)ON=C(C₉H₁₈)₂}]₂, show that the *cis* geometry of the starting complex is conserved in the products.

Introduction

Reactions where ketoximes or aldoximes, RR'C=NOH (R/R' = alkyl or aryl; R/R' = alkyl or aryl/H), behave as nucleophiles towards electrophilically activated ligands containing double and triple bonds are known although scarce,^{1–9} but recently this topic is being further developed by our studies.^{10–16} In particular, we observed an intriguing addition of oxime species to organonitriles in the platinum(IV) complexes *trans*-[PtCl₄(RCN)₂],¹³ giving stable *monodentate* iminoacylated ligands (**A** in Scheme 1) which can be considered as (alkylideneamino-oxy)imines. This iminoacylation reaction of the oximes was then rapidly extended to dialkylhydroxylamines¹⁴ and to *vic*-dioximes forming, in the latter case, after one-end addition, a novel type of metallaligands.¹⁵ The effect of the metal was also investigated and for the rhodium(III) nitrile complexes *mer*-[RhCl₃(RCN)₃]¹⁶ the coupling with cyclopentanone oxime led to *chelated* rather than *monodentate* species (**B** in Scheme 1).



Scheme 1

Our interest in further investigation of the iminoacylation of oximes is, so far, at least threefold. First, we wondered whether the results obtained for both platinum(IV) and rhodium(III) nitrile complexes and oximes were peculiar to these systems or whether the reactions are characteristic of other metal complexes. Secondly, we believe that factors which determine formation of monodentate (**A**) or bidentate (**B**) ligands

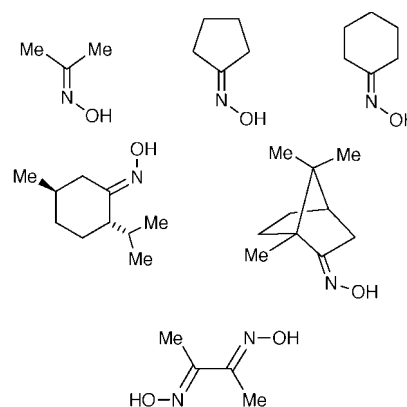


Fig. 1 Oximes employed in the coupling reaction.

(Scheme 1) deserve recognition and, in this context, extending the reaction to other systems is worthwhile. Thirdly, applying the iminoacylation reaction to different metal centers could also contribute to the establishment of the conditions for nucleophilic *versus* electrophilic activation of nitriles upon co-ordination. Of particular significance in this context would be the reaction of a nitrile complex of rhenium in a medium or *high oxidation state* allowing us to compare the observed behaviour of the ligating nitriles with that we have previously reported for [ReCl(RCN)(dippe)₂] (R = aryl, dippe = Ph₂PCH₂–CH₂PPh₂)^{17,18} in which the nitrile is activated towards electrophilic attack by the electron-rich *low oxidation state* rhenium(I) centre.

To extend the iminoacylation chemistry to another metal complex we chose for the current work the rhenium(IV) compound *cis*-[ReCl₄(MeCN)₂],¹⁹ studied its reactions with oximes which are depicted in Fig. 1 and the results obtained are reported herein.

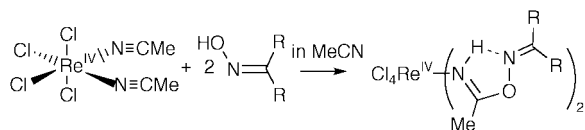
Results and discussion

The basic hypothesis for the current work is that electrophilic activation of an organonitrile can easily be achieved by its ligation to metal ions in high oxidation state. From this viewpoint the rhenium(IV) complex *cis*-[ReCl₄(MeCN)₂], whose synthesis and chemistry are well developed^{19–25} and structure is known (see footnote 9 in ref. 25), is a logical candidate for the study.

† Iminoacylation. Part 5, for Part 4 see ref. 16. *Supplementary data available*: rotatable 3-D crystal structure diagram in CHIME format. See <http://www.rsc.org/suppdata/dt/1999/4083/>

Moreover, it was demonstrated that the complex shows significant reactivity to either primary aromatic amines¹⁹ or amino-dialkylated adenines²⁵ and these reactions led to the insertion of the acetonitrile species in the N–H groups of the reagents giving iminoacylated species.

In accord with our expectations, the rhenium(IV) complex reacts rapidly with two equivalents of the oxime under mild conditions to afford the addition product in quantitative yield as shown in Scheme 2 for the case of the addition of monoximes.



Scheme 2

All compounds give satisfactory elemental analyses and they were also characterized by FAB⁺ mass spectrometry and IR spectroscopy. The IR spectra of the products show no bands due to $\nu(\text{C}\equiv\text{N})$ vibrations (except in the case of $[\text{ReCl}_4\{\text{NH}=\text{C}(\text{Me})\text{ON}=\text{C}(\text{C}_5\text{H}_{10})\}_2]\cdot\text{MeCN}$ which was isolated as the monoacetonitrile solvate, see below) but display very strong bands $\nu(\text{C}=\text{N})$ [$1609\text{--}1643\text{ cm}^{-1}$] and rather weak bands in ranges of $3260\text{--}3239$ and $1175\text{--}1207\text{ cm}^{-1}$ which can be attributed to $\nu(\text{N}\text{--}\text{H})$ and $\nu(\text{C}\text{--}\text{O})$ stretching vibrations,^{26,27} respectively. For the dimethylglyoxime addition product a characteristic intensive band due to $\nu(\text{O}\text{--}\text{H})$ stretch was detected at 3432 cm^{-1} . All these observed spectroscopic data are in good agreement with those found in cases of both platinum(IV) and rhodium(III) addition products, although in the former case the iminoacylated species, *i.e.* the (alkylideneaminoxy)imine ligands, display monodentate co-ordination¹³ and in the latter case bidentate.¹⁶

The complexes $\text{cis}-[\text{ReCl}_4\{\text{NH}=\text{C}(\text{Me})\text{ON}=\text{C}(\text{C}_5\text{H}_{10})\}_2]\cdot\text{MeCN}$ and $\text{cis}-[\text{ReCl}_4\{\text{NH}=\text{C}(\text{Me})\text{ON}=\text{C}(\text{C}_9\text{H}_{18})\}_2]$ were characterized by X-ray single-crystal diffraction study. The co-ordination polyhedron of both compounds is a slightly distorted octahedron with two iminoacyl ligands that are mutually *cis* (Figs. 2 and 3).

All values of the Re–Cl and Re–N distances, as well as the angles around the rhenium centre, agree well with those described for rhenium(IV) compounds in the literature.^{25,29} Both iminoacylated ligands adopt the *E* conformation and their geometry is similar to that found for the analogous ligand in $\text{trans}-[\text{PtCl}_4\{\text{NH}=\text{C}(\text{Me})\text{ON}=\text{C}(\text{C}_5\text{H}_{10})\}_2]$,¹³ C=N distances in the imino groups being slightly longer and the M–N=C angle slightly larger in the case of Re ($1.272\text{--}1.274\text{ \AA}/136.3\text{--}137.4^\circ$ for the former complex and $1.257\text{--}1.260\text{ \AA}/135.8\text{--}138^\circ$ for the latter one *vs.* $1.240\text{ \AA}/135.0^\circ$ for the platinum(IV) complex). In both imine ligands the imino hydrogen forms an intramolecular hydrogen bridge with the unco-ordinated oxime nitrogen. The distances and angles (N–H $0.70\text{--}0.76$, H \cdots N $2.14\text{--}2.28$, N \cdots N $2.58\text{--}2.60\text{ \AA}$, N–H \cdots N $110\text{--}118^\circ$ for the former complex and N–H $0.83\text{--}0.93$, H \cdots N $2.02\text{--}2.24$, N \cdots N $2.57\text{--}2.61\text{ \AA}$, N–H \cdots N $102\text{--}122^\circ$ for the latter one) are similar to those in previously described structures,^{13,14} where the same type of hydrogen bond was observed.

Most experimental data obtained show that the *trans* form is the more stable one for metal complexes in high oxidation states.^{30–32} Formation of the *cis* isomer in our case is probably due a rather low rate of *cis*-to-*trans* conversion of the rhenium(IV) iminoacylated species. However, this issue needs a separate study.

The oximes selectively react with the co-ordinated nitriles in $\text{cis}-[\text{ReCl}_4(\text{MeCN})_2]$ rather than with free acetonitrile (a solvent for the reaction), despite the incomparably higher concentration of the latter. Similar data were obtained for the amino-dialkylated adenines which add exclusively to acetonitrile species in $\text{cis}-[\text{ReCl}_4(\text{MeCN})_2]$ when the reaction is performed

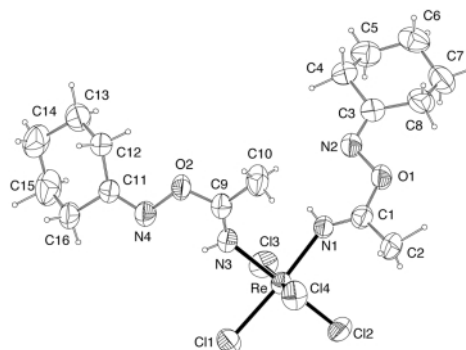


Fig. 2 A PLATON²⁸ drawing of *cis*- $[\text{ReCl}_4\{\text{NH}=\text{C}(\text{Me})\text{ON}=\text{C}(\text{C}_5\text{H}_{10})\}_2]\cdot\text{MeCN}$ with atomic numbering scheme (the solvent molecule is omitted for simplicity).

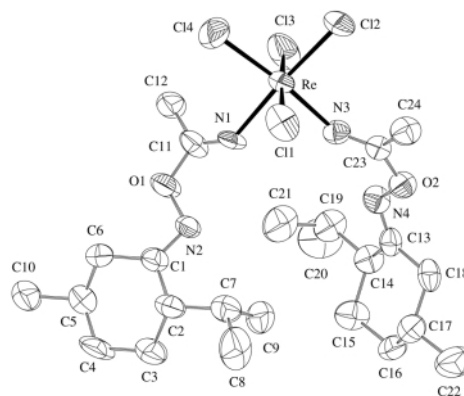


Fig. 3 A PLATON drawing of *cis*- $[\text{ReCl}_4\{\text{NH}=\text{C}(\text{Me})\text{ON}=\text{C}(\text{C}_9\text{H}_{18})\}_2]$ with atomic numbering scheme.

in MeCN.²⁵ Furthermore, our ¹H NMR experiment shows that the oximes do not react with acetonitrile under the reaction or even more harsh (56°C , 10 d) conditions and this gives an additional argument in favor of a metal-mediated pathway for the process.

This study also allows us to compare the types of activation of organonitriles by co-ordination at rhenium centres with the metal ion in quite different oxidation states, and with rather different π -electron releasing characters. In fact, we did not detect any reaction of the oxime with the nitrile ligating to the electron-rich rhenium(I) centre in $[\text{ReCl}(\text{NCR})(\text{dppe})_2]$, which exhibits a low value of the $\nu(\text{C}\equiv\text{N})$ stretching vibration in the IR spectrum (at a wavenumber lower than that observed in the free state by $40\text{--}130\text{ cm}^{-1}$) and is readily protonated, *e.g.* by HBF_4 or HCl , at the cyanocarbon to give the corresponding methyleneamide complexes $[\text{ReCl}(\text{N}=\text{CHR})(\text{dppe})_2]^+$.^{17,18} This process then provided the first example of activation, by co-ordination, of organonitriles towards *proton addition*, as well as a novel route to methyleneamide complexes, and was later extended by others³³ to the molybdenum(0) or tungsten(0) complexes $\text{trans}-[\text{M}(\text{N}_2)(\text{NCR})(\text{dppe})_2]$.

In contrast to this behaviour at an electron-rich metal site, which can be accounted for by a strong π -electron release ability of the metal to the organonitrile ligand, in the rhenium(IV) complex $[\text{ReCl}_4(\text{MeCN})_2]$ of the current study the organonitrile displays the IR $\nu(\text{C}\equiv\text{N})$ at a wavenumber (2289 cm^{-1}) that is higher than that of free acetonitrile (2254 cm^{-1})³⁴ and is activated towards nucleophilic addition by an oxime as a result of an extensive σ -electron donation of the nitrile to the relatively electron-poor metal ion without an appreciable π -electron back-bonding component of the co-ordination bond.

Experimental

Materials and instrumentation

Solvents were obtained from commercial sources and used as

received. The complex *cis*-[ReCl₄(MeCN)₂] was prepared from ReCl₅ (Alfa) and acetonitrile according to the published method.¹⁹ Oximes were purchased from Aldrich while menthione oxime [IUPAC name: (2*S*,5*R*)-5-methyl-2-(2-methylethyl)-cyclohexanone oxime] and camphor oxime [IUPAC name: (1*R*)-1,7,7-trimethylbicyclo[2.1.1]heptan-2-one oxime] were prepared in accord with known procedures.³⁵ The C, H and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. For TLC, Merck UV 254 SiO₂ plates have been used. Positive-ion FAB mass spectra were obtained on a Trio 2000 instrument by bombarding 3-nitrobenzyl alcohol matrices of the samples with 8 keV (*ca.* 1.28 × 10¹⁵ 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 3000MX instrument in KBr pellets.

Synthesis and characterization

The oxime (0.1 mmol) was added to a solution of *cis*-[ReCl₄(MeCN)₂] (20 mg, 0.05 mmol) in acetonitrile (0.5–0.6 mL) at 20–25 °C. The reaction mixture turned pale green almost immediately and was left to stand at room temperature for 2 h. In the case of 2-propanone, cyclopentanone and cyclohexanone oximes the released crystals were filtered off, washed with two 2 mL portions of acetonitrile and two 2 mL portions of diethyl ether and dried in air at room temperature. In case of the other oximes and dimethylglyoxime, precipitation is not observed and to isolate products the solvent was removed *in vacuo* at 20–25 °C. Yields were *ca.* 90%.

[ReCl₄{NH=C(Me)ON=CMe₂}₂]. Calc. for C₁₀H₂₀Cl₄N₄O₂Re: C, 21.6; H, 3.6; N, 10.1. Found: C, 21.6; H, 3.7; N, 10.0%. FAB⁺-MS: *m/z* 557, [M + H]⁺. mp = 111–112 °C (decomp.). TLC on SiO₂, R_f = 0.67 (eluent CH₂Cl₂). IR spectrum (selected bands), cm⁻¹: 3271mw, ν(N–H); 1632s and 1613s, ν(C=N); 1193w, ν(C–O).

[ReCl₄{NH=C(Me)ON=C(C₄H₈)₂}₂]. Calc. for C₁₄H₂₄Cl₄N₄O₂Re: C, 27.6; H, 4.0; N, 9.2. Found: C, 27.9; H, 4.0; N, 9.3%. FAB⁺-MS: *m/z* 574, [M – Cl]⁺. mp = 114–115 °C (decomp.). TLC on SiO₂, R_f = 0.79 (eluent CH₂Cl₂). IR spectrum (selected bands), cm⁻¹: 3260mw, ν(N–H); 1627s and 1609s, ν(C=N); 1174w, ν(C–O).

[ReCl₄{NH=C(Me)ON=C(C₅H₁₀)₂}₂·MeCN]. Calc. for C₁₈H₃₁Cl₄N₅O₂Re: C, 31.9; H, 4.6; N, 10.3. Found: C, 31.8; H, 4.5; N, 9.9%. FAB⁺-MS: *m/z* 636, [M + H]⁺. mp = 107–108 °C (decomp.). TLC on SiO₂, R_f = 0.85 (eluent CH₂Cl₂). IR spectrum (selected bands), cm⁻¹: 3265mw, ν(N–H); 2247vw, ν(C≡N); 1626s and 1611s, ν(C=N); 1186w, ν(C–O). Crystals of this complex for X-ray diffraction study were grown directly from the reaction mixture.

[ReCl₄{NH=C(Me)ON=C(C₉H₁₈)₂}₂]. Calc. for C₂₄H₄₄Cl₄N₄O₂Re: C, 38.5; H, 5.9; N, 7.5. Found: C, 39.4; H, 4.5; N, 7.3%. FAB⁺-MS: *m/z* 712, [M – Cl]⁺. mp = 130 °C (decomp.). TLC on SiO₂, R_f = 0.66 (eluent CHCl₃–C₆H₆, 5:1, v/v). IR spectrum (selected bands), cm⁻¹: 3254mw and 3239mw, ν(N–H); 1624s and 1610s, ν(C=N); 1186m, ν(C–O). Crystals of this complex for X-ray diffraction study were obtained directly from the reaction mixture on its evaporation (see above).

[ReCl₄{NH=C(Me)ON=C(C₉H₁₆)₂}₂]. Calc. for C₂₄H₄₀Cl₄N₄O₂Re: C, 38.7; H, 5.4; N, 7.5. Found: C, 38.8; H, 5.1; N, 7.2%. FAB⁺-MS: *m/z* 729, [M – CH₂]⁺. mp = 110 °C (decomp.). TLC on SiO₂, R_f = 0.65 (eluent CHCl₃). IR spectrum (selected bands), cm⁻¹: 3260mw, ν(N–H); 1633s and 1616s, ν(C=N); 1207m, ν(C–O).

[ReCl₄{NH=C(Me)ON=C(Me)C(Me)NOH}₂]. Calc. for C₁₂H₂₂Cl₄N₆O₄Re: C, 22.4; H, 3.5; N, 13.1. Found: C, 22.7; H, 3.9; N, 13.0%. FAB⁺-MS: *m/z* 606, [M – Cl]⁺. mp = 122 °C (decomp.). TLC on SiO₂, two spots with approximately equal intensity probably due to either *cis-trans* isomers or *syn-anti* conformers,¹⁵ R_f = 0.30 and 0.51 (eluent acetone–chloro-

Table 1 Crystal data and structure refinement for *cis*-[ReCl₄{NH=C(Me)ON=C(C₅H₁₀)₂}₂·MeCN **1** and *cis*-[ReCl₄{NH=C(Me)ON=C(C₉H₁₈)₂}₂ **2**

	1	2
Empirical formula	C ₁₈ H ₃₁ Cl ₄ N ₅ O ₂ Re	C ₂₄ H ₄₄ Cl ₄ N ₄ O ₂ Re
Formula weight	677.48	748.64
<i>T</i> /K	293(2)	293(2)
Crystal system, space group	Monoclinic, <i>P</i> ₂ / <i>c</i> (no 14)	Orthorhombic, <i>P</i> ₂ ₁ ₂ ₁ (no 19)
<i>a</i> /Å	10.465(2)	9.890(2)
<i>b</i> /Å	25.267(5)	16.460(3)
<i>c</i> /Å	10.905(2)	19.921(4)
β/°	112.21(3)	
<i>V</i> /Å ³	2669.5(9)	3242.9(11)
<i>Z</i>	4	4
<i>D</i> _c /Mg m ⁻³	1.686	1.533
μ(Mo-Kα)/mm ⁻¹	4.975	4.102
Reflections collected/unique	3620/3430 [R(int) = 0.0414]	1662/1662 [R(int) = 0.0]
Final <i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)] (all data)	0.0254, 0.0677 0.0254, 0.0677	0.0292, 0.0743 0.0292, 0.0743

Table 2 Bond lengths (Å) and angles (°) for *cis*-[ReCl₄{NH=C(Me)ON=C(C₅H₁₀)₂}₂·MeCN

Re–N(1)	2.090(6)	C(1)–C(2)	1.480(10)
Re–N(3)	2.101(4)	C(9)–C(10)	1.487(11)
Re–Cl(1)	2.3320(18)	C(3)–C(4)	1.505(9)
Re–Cl(2)	2.3211(16)	C(4)–C(5)	1.516(11)
Re–Cl(3)	2.3348(16)	C(5)–C(6)	1.507(12)
Re–Cl(4)	2.3265(16)	C(6)–C(7)	1.533(14)
N(1)–C(1)	1.272(8)	C(7)–C(8)	1.522(13)
N(3)–C(9)	1.274(8)	C(8)–C(3)	1.471(11)
O(1)–C(1)	1.334(8)	C(11)–C(12)	1.480(9)
O(2)–C(9)	1.337(6)	C(12)–C(13)	1.514(10)
O(1)–N(2)	1.465(6)	C(13)–C(14)	1.520(15)
O(2)–N(4)	1.458(7)	C(14)–C(15)	1.517(16)
N(2)–C(3)	1.260(9)	C(15)–C(16)	1.515(13)
N(4)–C(11)	1.275(7)	C(16)–C(11)	1.494(11)
N(1)–Re–N(3)	89.4(2)	O(1)–C(1)–C(2)	110.4(7)
N(1)–Re–Cl(1)	175.00(14)	O(2)–C(9)–C(10)	111.2(6)
N(1)–Re–Cl(2)	90.53(15)	C(1)–O(1)–N(2)	112.2(4)
N(1)–Re–Cl(3)	85.55(14)	C(9)–O(2)–N(4)	111.5(5)
N(1)–Re–Cl(4)	92.76(15)	O(1)–N(2)–C(3)	109.9(5)
N(3)–Re–Cl(1)	86.91(15)	O(2)–N(4)–C(11)	109.8(5)
N(3)–Re–Cl(2)	178.76(12)	N(2)–C(3)–C(4)	114.6(5)
N(3)–Re–Cl(3)	86.12(13)	N(4)–C(11)–C(12)	128.9(6)
N(3)–Re–Cl(4)	88.68(13)	N(2)–C(3)–C(8)	128.1(6)
Cl(1)–Re–Cl(2)	93.09(7)	N(4)–C(11)–C(16)	114.7(6)
Cl(1)–Re–Cl(3)	90.84(7)	C(3)–C(4)–C(5)	111.3(6)
Cl(1)–Re–Cl(4)	90.52(7)	C(4)–C(5)–C(6)	111.6(7)
Cl(2)–Re–Cl(3)	92.65(6)	C(5)–C(6)–C(7)	110.7(7)
Cl(2)–Re–Cl(4)	92.56(6)	C(6)–C(7)–C(8)	112.3(7)
Cl(3)–Re–Cl(4)	174.54(7)	C(7)–C(8)–C(3)	112.2(7)
C(1)–N(1)–Re	136.3(4)	C(11)–C(12)–C(13)	110.6(6)
C(9)–N(3)–Re	137.4(4)	C(12)–C(13)–C(14)	111.8(9)
N(1)–C(1)–O(1)	123.1(5)	C(13)–C(14)–C(15)	110.3(8)
N(3)–C(9)–O(2)	123.0(5)	C(14)–C(15)–C(16)	110.7(8)
N(1)–C(1)–C(2)	126.5(8)	C(15)–C(16)–C(11)	109.2(7)
C(3)–C(9)–C(10)	125.9(5)		

form = 1:4, v/v). IR spectrum (selected bands), cm⁻¹: 3432s, ν(O–H); 3257mw, ν(N–H); 1644s and 1619s, ν(C=N); 1196w, ν(C–O).

Structure determination of *cis*-[ReCl₄{NH=C(Me)ON=C(C₅H₁₀)₂}₂·MeCN and *cis*-[ReCl₄{NH=C(Me)ON=C(C₉H₁₈)₂}₂]

Emerald prisms of *cis*-[ReCl₄{NH=C(Me)ON=C(C₅H₁₀)₂}₂·MeCN and bluish prisms of *cis*-[ReCl₄{NH=C(Me)ON=C(C₉H₁₈)₂}₂] were grown directly from the reaction mixtures. Diffraction data were collected on an Enraf-Nonius CAD 4 diffractometer. Data processing was performed with the program PROFIT.³⁶ The structures were solved by standard

Table 3 Bond lengths (Å) and angles (°) for *cis*-[ReCl₄{NH=C(Me)ON=C(C₉H₁₈)₂}

Re–N(1)	2.121(9)	C(3)–C(4)	1.49(2)
Re–N(3)	2.108(10)	C(4)–C(5)	1.509(19)
Re–Cl(1)	2.339(5)	C(5)–C(6)	1.525(19)
Re–Cl(2)	2.317(4)	C(6)–C(1)	1.51(2)
Re–Cl(3)	2.316(4)	C(2)–C(7)	1.53(2)
Re–Cl(4)	2.318(5)	C(7)–C(8)	1.52(2)
N(1)–C(11)	1.260(17)	C(7)–C(9)	1.53(2)
N(3)–C(23)	1.257(16)	C(5)–C(10)	1.54(2)
O(1)–C(11)	1.351(14)	C(13)–C(14)	1.477(18)
O(2)–C(23)	1.344(15)	C(14)–C(15)	1.57(2)
O(1)–N(2)	1.468(13)	C(15)–C(16)	1.49(2)
O(2)–N(4)	1.469(13)	C(16)–C(17)	1.56(2)
N(2)–C(1)	1.283(15)	C(17)–C(18)	1.51(2)
N(4)–C(13)	1.270(18)	C(18)–C(13)	1.517(19)
C(11)–C(12)	1.490(18)	C(14)–C(19)	1.50(2)
C(23)–C(24)	1.451(18)	C(19)–C(20)	1.52(3)
C(1)–C(2)	1.503(18)	C(19)–C(21)	1.54(3)
C(2)–C(3)	1.57(2)	C(17)–C(22)	1.55(2)
N(1)–Re–N(3)	83.7(4)	C(1)–C(2)–C(3)	106.5(12)
N(1)–Re–Cl(1)	83.8(3)	C(2)–C(3)–C(4)	112.2(14)
N(1)–Re–Cl(2)	174.9(3)	C(3)–C(4)–C(5)	113.1(11)
N(1)–Re–Cl(3)	92.1(3)	C(4)–C(5)–C(6)	110.0(12)
N(1)–Re–Cl(4)	89.8(3)	C(5)–C(6)–C(1)	109.9(12)
N(3)–Re–Cl(1)	88.3(3)	C(6)–C(1)–N(2)	126.1(11)
N(3)–Re–Cl(2)	93.3(3)	C(1)–C(2)–C(7)	114.0(11)
N(3)–Re–Cl(3)	85.2(3)	C(2)–C(7)–C(8)	109.7(13)
N(3)–Re–Cl(4)	173.3(3)	C(2)–C(7)–C(9)	115.0(13)
Cl(1)–Re–Cl(2)	92.08(16)	C(3)–C(2)–C(7)	113.7(13)
Cl(1)–Re–Cl(3)	172.68(16)	C(4)–C(5)–C(10)	113.3(11)
Cl(1)–Re–Cl(4)	92.20(16)	C(6)–C(5)–C(10)	110.0(13)
Cl(2)–Re–Cl(3)	91.69(15)	N(4)–C(13)–C(14)	117.0(12)
Cl(2)–Re–Cl(4)	93.33(16)	C(13)–C(14)–C(15)	126.3(11)
Cl(3)–Re–Cl(4)	93.84(18)	C(14)–C(15)–C(16)	112.0(11)
C(11)–N(1)–Re	135.8(8)	C(15)–C(16)–C(17)	111.2(13)
C(23)–N(3)–Re	138.0(9)	C(16)–C(17)–C(18)	110.8(12)
N(1)–C(11)–O(1)	123.1(11)	C(17)–C(18)–C(13)	111.9(12)
N(3)–C(23)–O(2)	122.0(11)	C(18)–C(13)–N(4)	125.9(12)
N(1)–C(11)–C(12)	127.9(11)	C(13)–C(14)–C(19)	115.2(13)
N(3)–C(23)–C(24)	126.4(12)	C(14)–C(19)–C(20)	116.2(14)
C(11)–O(1)–N(2)	111.9(9)	C(14)–C(19)–C(21)	111.1(16)
C(23)–O(2)–N(4)	111.5(9)	C(15)–C(14)–C(19)	113.6(12)
O(1)–N(2)–C(1)	110.0(10)	C(16)–C(17)–C(22)	109.9(13)
O(2)–N(4)–C(13)	112.3(10)	C(18)–C(17)–C(22)	109.7(12)
C(8)–C(7)–C(9)	110.2(16)	C(2)–C(1)–C(6)	115.1(11)
O(1)–C(11)–C(12)	108.9(10)	C(20)–C(19)–C(21)	109.0(16)
C(14)–C(13)–C(18)	117.1(12)	O(2)–C(23)–C(24)	111.6(10)
N(2)–C(1)–C(2)	118.7(12)		

Patterson methods (SHELXTL package³⁷) and refined by full-matrix least squares based on F^2 using SHELX-97.³⁸ In the case of *cis*-[ReCl₄{NH=C(Me)ON=C(C₉H₁₈)₂}]₂ a comparatively low ratio of observed reflections to number of parameters (1662:316) was used due to poor crystal quality. Extinction correction, Lorentz, polarization and absorption corrections were made.³⁹ Scattering factors from ref. 40. Crystal data are given in Table 1, bond distances and angles in Tables 2 and 3.

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See <http://www.rsc.org/suppdata/dt/1999/4083/> for crystallographic files in .cif format.

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