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Rhenium(V) complexes with tridentate *P*,*N*,*S* ligands

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1. Introduction

Tri-, tetra- or multiple-dentate ligands, which form stable or kinetically inert complexes with rhenium and technetium are still of interest for nuclear medical labeling procedures, since previous studies have shown that mono- and bidentate ligand systems may suffer from insufficient in vivo stability due to rapid ligand exchange reactions with plasma components [1–5]. For common technetium(V) and rhenium(V) cores, ligands with 'medium' and 'soft' donor atoms are recommended [1,2]. Thus, chelators with a mixed phosphorus, sulfur and nitrogen donor sphere should be very suitable. However, there is surprisingly less known about rhenium or technetium complexes with such ligands. One example has been extensively studied. It is a thiolato-substituted amide, which has been prepared by a reaction of N-[2-(diphenylphosphanyl)]benzoyloxylsuccinimide with S-(triphenylmethyl)-2-aminoethanethiol [6,7]. A more facile synthesis of P,N,S ligands is possible following a general procedure, which has been applied to various ligands including amino acid derivatives: reactions between N-(dialkyl)thiocarbamoylbenzimidoyl chlorides with substituted amines [8-13].

Since the first syntheses of *N*-(dialkyl)thiocarbamoylbenzimidoyl chlorides and their reaction products with primary amines, *N*-(dialkyl)thiocarbamoylbenzamidines [14,15], a large number of different transition metal complexes with such ligands were synthesized and extensively studied [16]. For a long time, however, this ligand system was restricted to bidentate ligands (*S*,*N* type ligands of Scheme 1). Recently, we extended the denticity of these

ABSTRACT

Novel, potentially tridentate ligands with *P*,*N*,*S* donor sets (HL^{diethyl} and HL^{morph}) were prepared from reactions of *N*-(dialkyl)thiocarbamoylbenzimide chlorides with 2-(diphenylphosphinomethyl)aniline. They readily react with (NBu₄)[ReOCl₄] under formation of air-stable [ReOCl₂(L^R)] complexes, in which the tridentate ligands coordinate meridionally. A similar coordination mode is observed in the nitridorhenium(V) complex [ReN(OReO₃)(PPh₃)(L^{diethyl})], which can be obtained from a reaction of [ReNCl₂(PPh₃)₂] and HL^{diethyl}. The complexes were characterized spectroscopically and by X-ray structure analyses. © 2011 Elsevier Ltd. All rights reserved.

> ligands up to four, so that nowadays *N*-(dialkyl)thiocarbamoylbenzamidines with *S*,*N*,*N*, *S*,*N*,*O*, *S*,*N*,*S* and *S*,*N*,*N*,*S* donor sets are available (Scheme 1), and their coordination chemistry with rhenium and is under study [8–13,17]. These compounds are known for a high flexibility in their donor functions and peripheral substituents as well as the formation of stable chelates with a number of metal ions.

POLYHEDRON

As part of our systematic work in the synthesis of phosphinecontaining ligands for rhenium and technetium, we report in the present work about reactions of 2-(diphenylphosphinomethyl)aniline with *N*-(dialkyl)thiocarbamoylbenzimidoyl chlorides, which yield potentially tridentate *P*,*N*,*S* ligands. Furthermore, we report about their coordination behavior towards oxorhenium(V) and nitridorhenium(V) centers.

2. Results and discussion

Reactions of 2-(diphenylphosphinomethyl)aniline with substituted thiocarbamoylbenzimidoyl chlorides in tetrahydrofurane (Eq. (1)) give the tridentate ligands in good yields. Small amount (approximately 5%) of impurities due the formation of the corresponding phosphine oxides are formed during these reactions. They can be removed by subsequent recrystallization under anaerobic conditions in order to obtain the pure products. For complex formation with Re(V) compounds, however, the crude products can be used without purification, since the impurities have no influence on the desired complex formation and potential sideproducts such as phosphine oxide complexes do not play a role as long as a slight excess of the ligands is applied.

The ${}^{31}P{}^{1}H$ NMR spectra of $HL^{diethyl}$ and HL^{morph} reveal each one singlet at -17.3 ppm ($HL^{diethyl}$) and -16.9 ppm (HL^{morph}).



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¹H NMR spectra indicate hindered rotation around the C–N(alkyl) bonds, which can clearly be seen from the splitting patterns of the methylene and methyl signals of the morpholine and diethyl substituents. This is a common feature of the NMR spectra of this type of ligands and analogous coupling patterns were already described for similar thiocarbamoylbenzamidines. The IR spectra clearly show the vibration of the NH bonds at 3337 cm⁻¹ (HL^{morph}) and 3325 cm⁻¹ (HL^{diethyl}). Broad bands for the CN bonds are found at 1628 cm⁻¹ (HL^{morph}) and 1612 cm⁻¹ (HL^{diethyl}).

Reactions of HL^R with (NBu₄)[ReOCl₄] result in green precipitates or crystals. The products have the composition [ReOCl₂(L^R)] (Eq. (2)). The organic ligand is single deprotonated and coordinates meridionally tridentate in the equatorial coordination sphere of rhenium via the phosphorus, nitrogen and sulfur donor atoms. The remaining two positions are occupied by chlorido ligands.

The ³¹P{¹H} NMR spectra of both compounds each show a singlet. The signals appear at 5.7 ppm for [ReOCl₂(L^{diethyl})] and at 7.1 ppm for [ReOCl₂(L^{morph})]. This indicates a low-field shift of more than 20 ppm with respect to the signals observed in the spectra of the non-coordinated ligands, and confirms the presence of only one phosphorus atom in the complexes. The ¹H NMR spectra of both compounds are complex, which is due to hindered rotation around the C-NR¹R² bonds as has already been described for the uncoordinated benzamidines HL^{diethyl} and HL^{morph}. This feature is also common for metal complexes with thiocarbamoylbenzamidines and leads to a splitting of the signals of the alkyl groups of the diethyl and morpholine substituents. Two multiplets can be assigned to the two methyl groups at 1.38 ppm in the case of $(L^{\tilde{diethyl}})^{-}$, whereas the two methylene groups in this ligand are splitted into four signals at 3.58, 3.81, 4.49 and 4.99 ppm. In case of (L^{morph})⁻, five multiplets at 3.80, 4.21, 4.39, 4.75 and 5.20 ppm can be assigned to the methylene groups of the morpholine substituent. The methylene protons adjacent to the phosphorus atoms produce multiplets at 4.28 ppm ([ReOCl₂(L^{diethyl})]) and 4.39 ppm ([ReOCl₂(L^{morph})], respectively. The latter one overlaps with a signal of one of the methylene groups of the morpholine substituent.

The IR spectra of both complexes confirm the deprotonation of the organic ligands by the absence of $v_{\rm NH}$ vibrations. Strong, broad bands can be assigned to the C=N double bonds of the organic ligands in both cases. Both bands, which are found at 1523 cm⁻¹ for [ReOCl₂(L^{diethyl})] and at 1512 cm⁻¹ for [ReOCl₂(L^{morph})] are bathochromically shifted by approximately 100 cm⁻¹ with respect to HL^{diethyl} and HL^{morph}. These shifts indicate chelate formation with a large degree of π -electron delocalization within the chelate rings.

Crystals suitable for X-ray diffraction were obtained by crystallization from a mixture of $CH_2Cl_2/acetone$ or pure acetone. [Re- $OCl_2(L^{diethyl})$] crystallizes in the orthorhombic space group *Fdd2*



Fig. 1. Ellipsoid representation [31] of the molecular structure of (a) [ReO-Cl₂-(L^{diethyl})] and (b) [ReOCl₂(L^{morph})]. Thermal ellipsoids represent 50% probability. H atoms have been omitted for clarity.

Table 1 Selected bond lengths (Å) and angles (°) in $[ReOCl_2(L^{diethyl})]$ and $[ReOCl_2(L^{morph})]$.

	[ReOCl ₂ (L ^{diethyl})]	[ReOCl ₂ (L ^{morph})]
Re1-010	1.685(4)	1.671(6)
Re1-C11	2.401(2)	2.399(2)
Re1-C12	2.466(2)	2.482(2)
Re1-S1	2.344(2)	2.333(2)
Re1-N5	2.084(5)	2.086(7)
Rel-P1	2.461(2)	2.452(2)
C2-N3	1.328(8)	1.33(2)
C2-N51	1.330(7)	1.330(7)
N3-C4	1.316(7)	1.32(2)
C4-N5	1.356(7)	1.36(2)
N5-C16	1.424(7)	1.44(2)
N5-Rel-CH	169.4(7)	170.1(2)
SI-Rel-PI	163.80(5)	164.48(9)
O10-Rel-C12	163.3(2)	166.8(2)
C11-Rel-C12	87.92(5)	87.55(9)

with one molecule in the asymmetric unit, whereas $[\text{ReOCl}_2-(L^{\text{morph}})]$ crystallizes in the monoclinic space group $P_{2_1/c}$ with one complex molecule and two molecules of solvent acetone in the asymmetric unit. Ellipsoid representations of the complex molecules are shown in Fig. 1. Selected bond lengths and angles for both compounds are given in Table 1.

The *trans* influence of the oxo ligand lengthens the Re–Cl2 bonds to values of 2.466(2) and 2.482(2) Å, respectively, in comparison to approximately 2.40 Å for the Re1–Cl1 bonds in the equatorial coordination spheres. Inside the organic ligands, a bond

length equalization of the C2–N3, C2–N51, N3–C4 and C4–N5 bonds is observed. All these bonds show partial double bond character with bond lengths between 1.32(2) and 1.36(2) Å. By the fact that the C2–N51 bond is involved in this π -electron delocalization, the hindered rotation, which is detected in the NMR spectra, can readily be explained.

With regard to the completely identical reaction patterns of $HL^{diethyl}$ and HL^{morph} with the oxorhenium(V) core, only the reaction of $HL^{diethyl}$ with the common nitridorhenium(V) precursor [ReNCl₂(PPh₃)₂] was studied in order to give information about the products formed with the nitridorhenium(V) core.

The reaction of HL^{diethyl} with [ReNCl₂(PPh₃)₂] was performed in CH₂Cl₂. The sparingly soluble starting complex rapidly dissolves after the addition of the phosphinobenzamidine and a supporting base such as NEt₃. An attempted reaction without the supporting base did not show any formation of a ligand exchange product within 1 h due to the low solubility of the starting complex. The product could be isolated as orange-brown crystals after overlayering the reaction solution with methanol. X-ray crystal structure determination showed the formation of a nitridorhenium(V) chelate of the composition [ReN(OReO₃)(PPh₃)(L^{diethyl})]. An ellipsoid representation of this complex is depicted in Fig. 2 and selected bond lengths and angles are listed in Table 2. The coordination sphere of Re1 can be best described as a distorted octahedron. The thiocarbamoylbenzamidine coordinates meridionally tridentate to the Re(V) center after single deprotonation. The equatorial coordination plane of the complex is completed by one molecule triphenylphosphine, whereas the axial positions are occupied by one nitrido ligand N10 and a perrhenato ligand.

The reproducible formation and coordination of perrhenate in the product was unexpected, but is not unusual in the coordination chemistry of rhenium. It is frequently observed, when ReO_4^- is formed as a side-product of the complex formation and an additional mononegative ligand is required for charge compensation [17–23].

The bond between Re1 and O1 of 2.348(5) Å is remarkably long for a ReO single bond. This is due to the strong *trans* influence of the triple-bonded nitrido ligand. The Re2–O1 bond length of 1.734(5) Å is slightly lengthened as a consequence of the coordination, while the Re2–O2, Re2–O3 and Re2–O4 bonds clearly show



Fig. 2. Ellipsoid representation [31] of the molecular structure of $[ReN-(OReO_3)-(PPh_3)-(L^{diethyl})]$. Thermal ellipsoids represent 50% probability. H atoms have been omitted for clarity.

Table 2

Selected bond lengths (Å) and angles (°) in [ReN(OReO₃)(PPh₃)(L^{diethyl})].

Re1-N10	1.654(6)	S1-C2	1.736(7)	Re2-02	1.708(8)
Re1-P1	2.448(2)	C2-N51	1.33(1)	Re2-03	1.688(9)
Re1-N5	2.150(5)	C2-N3	1.330(9)	Re2-04	1.709(5)
Re1-S1	2.369(2)	N3-C4	1.327(9)	N10-Re1-01	173.4(2)
Rel-O1	2.348(5)	C4-N5	1.321(9)	Re1-01-Re2	151.0(3)
Re1-P2	2.433(2)	Re2-01	1.734(5)	P1-Re1-P2	96.87(6)

double bond character with bond lengths between 1.688(9) and 1.709(5) Å. The Re1–O1–Re2 bond is bent with an angle of 151.0(3)°. This bonding situation is common for perrhenato ligands [17–23]. In the present case, there was no evidence for the formation of a square-planar or trigonal-bipyramidal, cationic [Re-N(PPh₃)(L^{diethyl})]⁺ complex or a species of the composition [ReN(PPh₃)Cl(L^{diethyl})]. Explicit experiments in order to exchange the weakly bonded perrhenato ligand have not been undertaken.

The ³¹P{¹H} NMR spectrum of [ReN(OReO₃)(PPh₃)(L^{diethyl})] reveals two signals at 21.6 and 46.0 ppm, which can be assigned to phosphorus atoms of $(L^{diethyl})^{-}$ and PPh₃, respectively. The ¹H NMR spectrum of the compound is complex as those of the oxorhenium(V) chelates. It shows splittings of the signals of the methylene and methyl protons of the diethyl substituents of the organic ligand as was discussed for [ReOCl₂(L^{diethyl})]. One multiplet at 4.28 ppm can be assigned to the methylene group next to the phosphorus atom. Deprotonation and coordination of the amino group can be concluded from the absence of the NH NMR signal. The IR spectrum confirms this fact as well by the absence of a $v_{\rm NH}$ band. A shift of the $v_{\rm CN}$ band by 140 cm⁻¹ to lower wave numbers with respect to uncoordinated HL^{diethyl} is due to the coordination of the ligand. A band of medium intensity at 1072 cm⁻¹ can be assigned to the ReN triple bond. Two intense bands at 921 and 860 cm⁻¹ result from the coordinated perrhenate, which normally can be identified by two or three IR bands in the range of 930-860 cm⁻¹ depending on the symmetry of the coordination mode [24].

The origin of the perrhenate ligand is doubtlessly a hydrolytic oxidation during the complex formation. The yields, which are obtained, are reproducibly higher than 50% with regards to Re, which is by far too high to be explained by some impurities in the starting material [ReNCl₂(PPh₃)₂], which has additionally be excluded by careful inspection of the IR spectrum of this precursor. The formation of perrhenate from a nitrido compound is unexpected, but not without precedent. Some reactions are reported, where chlorido ligands of [ReNCl₂(PMe₂Ph)₃] or [ReNCl₂(PPh₃)₂] were abstracted after the addition of base and the 'undercoordinated' metal ion was stabilized by subsequent oxidation and hydrolysis, which finally results in the formation of perrhenate [21,22]. In some rare cases, the isolation and structural characterization of compounds containing one important intermediate of such reactions, trioxidonitridorhenate(VII) (ReO₃N)²⁻, succeeded [25,26]. This building block readily hydrolyses under the formation of perrhenate.

Summarizing, it can be stated that the new tridentate phosphines HL^{diethyl} and HL^{morph} are suitable as mononegative ligands and form stable oxorhenium(V) and nitridorhenium(V) complexes.

3. Experimental

(NBu₄)[ReOCl₄] [27], [ReNCl₂(PPh₃)₂] [28], and 2-(diphenylphosphinomethyl)aniline H_2L^1 [29] were prepared by literature procedures. IR spectra were measured as KBr pellets on a Shimadzu FTIR-spectrometer 8300. ESI mass spectra were measured with an Agilent 6210 ESI-TOF. All MS results are given in the form: m/z, assignment. Elemental analysis of carbon, hydrogen, nitrogen, and sulfur were determined using a Heraeus vario EL elemental analyzer. NMR spectra were taken with a JEOL 400 MHz multinuclear spectrometer.

3.1. HL^{diethyl}

A solution of NEt₃ (280 μ L, 2 mmol) in 2 mL THF was added to a solution of 2-(diphenylphosphinomethyl)aniline (582 mg, 2 mmol) and diethylthiocarbamoylbenzimidoyl chloride (509 mg, 2 mmol) in 3 mL THF under an atmosphere of dry argon at 0 °C under vigorous stirring. After 1 h, the reaction mixture was heated to 50 °C and stirred for another 1.5 h. The resulting triethylammonium chloride was filtered off and the solvent was removed in vacuum. Ethanol was added to the remaining residue under vigorous stirring. This gave a pale yellow powder, which was filtered off and dried under vacuum. Yield: 78% (800 mg). Anal. Calc. for C₃₁H₃₂N₃SP: C, 73.06; H, 6.33; N, 8.24; S, 6.29. Found: C, 72.59; H, 5.96; N, 7.94; S, 5.93%. IR (ν_{max} , cm⁻¹): 3325 w (N–H), 1612 st (C=N). ¹H NMR (DMSO, δ . ppm): 1.13 (t, 3H, CH₃, J = 6.9 Hz), 1.18 (t, 3H, CH₃, J = 7.1 Hz), 3.69 (q, 2H, CH₂, J = 6.9 Hz), 3.77 (s, 2H, PCH₂), 3.85 (q, 2H, CH₂, *I* = 7.1 Hz), 6.96–7.15 (m, 4H, Ph), 7.41–7.63 (m, 14H, Ph), 10.17 (s, 1H, NH). ³¹P NMR (CDCl₃, δ , ppm): -17.3. +ESI MS (m/z): 508.20 [M+H]+.

3.2. HL^{morph}

The compound was prepared as described for HL^{diethyl} by using morpholinylthiocarbamoylbenzimidoyl chloride (538 mg, 2 mmol) instead of the diethyl derivative. Yield: 86% (900 mg). *Anal.* Calc. for C₃₁H₃₀N₃SOP: C, 71.11; H, 5.77; N, 8.02; S, 6.12. Found: C, 70.76; H, 5.43; N, 7.73; S, 5.85%. IR (ν_{max} , cm⁻¹): 3337 w (N–H), 1628 st (C=N). ¹H NMR (DMSO, δ , ppm): 3.52 (t, 2H, CH₂, *J* = 4.4 Hz), 3.57 (t, 2H, CH₂, *J* = 4.4 Hz), 3.94 (t, 2H, CH₂, *J* = 4.4 Hz), 6.96–7.11 (m, 4H, Ph), 7.32–7.52 (m, 15H, Ph), 9.99 (s, 1H, NH). ³¹P NMR (CDCl₃, δ , ppm): –16.9. +ESI MS (*m*/*z*): 524.19 [M+H]⁺, 546.18 [M+Na]⁺, 563.17 [M+K]⁺.

3.3. [$ReOCl_2(L^{diethyl})$]

 $\rm HL^{diethyl}$ (51 mg, 0.1 mmol) dissolved in 2 mL CH₂Cl₂ was added to a solution of (NBu₄)[ReOCl₄] (59 mg, 0.1 mmol) in 2 mL CH₂Cl₂. The solution immediately became emerald green. It was stirred for 2 h at room temperature. Acetone (4 mL) was added and the mix-

Table 3X-ray structure data collection and refinement parameters.

ture was kept for crystallization. The product deposited as emerald green crystals. Yield (based on Re): 58% (45 mg). *Anal.* Calc. for C₃₁H₃₁Cl₂N₃OSPRe: C, 47.63; H, 4.00; N, 5.38; S, 4.10. Found: C, 47.52; H, 3.67; N, 5.16; S, 4.08%. IR (ν_{max} , cm⁻¹): 1523 st (C=N), 968 st (Re=O). ¹H NMR (CDCl₃, δ , ppm): 1.38 (m, 6H, 2CH₃), 3.58 (m, 1H, NCH₂), 3.81 (m, 1H, NCH₂), 4.28 (m, 2H, PCH₂), 4.49 (m, 1H, NCH₂), 4.99 (m, 1H, NCH₂), 6.59–7.62 (m, 19H, Ph). ³¹P NMR (CDCl₃, δ , ppm): 5.7. +ESI MS (*m*/*z*): 742.17 [M–2Cl+OMe]⁺.

3.4. $[ReOCl(L^{morph})]$

HL^{morph} (52 mg, 0.1 mmol) was added to a solution of (NBu₄)-[ReOCl₄] (59 mg, 0.1 mmol) in 4 mL methanol. A deep green solution was obtained immediately, which was stirred at room temperature until the product precipitated as a green solid. Crystals, which were suitable for X-ray crystallography, were obtained from acetone. Yield (based on Re): 58% (45 mg). *Anal.* Calc. for C₃₁H₂₉Cl₂N₃OSPRe: C, 46.79; H, 3.67; N, 5.28; S, 4.03. Found: C, 46.93; H, 3.12; N, 5.41; S, 4.27%. IR (ν_{max} , cm⁻¹): 1512 st (C=N), 972 st (Re=O). ¹H NMR (DMSO, δ , ppm): 3.80 (m, 4H, 2CH₂), 4.21 (m, 2H, NCH₂), 4.39 (m, 4H, PCH₂, NCH₂), 4.75 (m, 1H, CH₂), 5.20 (m, 1H, NCH₂), 6.53 (m, 1H, Ph), 6.69 (m, 1H, Ph), 7.23–7.99 (m, 17H, Ph). ³¹P NMR (CDCl₃, δ , ppm); 7.1. +ESI-MS (*m*/*z*): 756.14 [M–2Cl+OMe]+.

3.5. [ReN(OReO₃)(PPh₃)(L^{diethyl})]

A solution of HL^{diethyl} (51 mg, 0.1 mmol) in 5 mL CH₂Cl₂ was dropwise added to a suspension of [ReNCl₂(PPh₃)₂] (80 mg, 0.1 mmol) in 5 mL CH₂Cl₂. After stirring for 1 h at room temperature, three drops NEt₃ were added. An orange-brown solution was obtained after stirring for two more hours. For crystallization, the solution was overlayered with methanol. The product was isolated as orange-brown crystals. Yield (based on Re): 57% (35 mg). *Anal.* Calc. for C₄₉H₄₆N₄O₄SP₂Re₂: C, 48.18; H, 3.79; N, 4.59; S, 2.63. Found: C, 47.93; H, 3.30; N, 4.21; S, 2.93%. IR (ν_{max} , cm⁻¹): 1473 st (C=N), 1095 st (Re=N), 921 st, 860 st (ReO₄⁻). ¹H NMR (CDCl₃, δ , ppm): 1.34 (m, 6H, 2CH₃), 3.59 (m, 1H, NCH₂), 4.28 (m, 2H, PCH₂), 4.51 (m, 1H, NCH₂), 4.98 (m, 1H, NCH₂), 6.43–7.94 (m, 19H, Ph). ³¹P NMR (CDCl₃, δ , ppm): 21.6, 46.0. +ESI-MS (m/z): 971.25 [M–ReO₄]⁺, 1221.19 [M+H]⁺, 1243.19 [M+Na]⁺.

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	[ReOCl ₂ (L ^{diethyl})]	[ReOCl ₂ (L ^{morph})]·2acetone	$[\text{ReN}(\text{OReO}_3)(\text{PPh}_3)(\text{L}^{\text{diethyl}})] \cdot 0.5\text{CH}_2\text{Cl}_2$
Formula	C ₃₁ H ₃₁ Cl ₂ N ₃ OSPRe	C ₃₇ H ₄₁ Cl ₂ N ₃ O ₄ SPRe	C _{49.5} H ₄₇ CIN ₄ O ₄ P ₂ SRe
Mw	781.49	911.86	1263.76
Crystal system	orthorhombic	monoclinic	triclinic
a (Å)	33.318(2)	15.281(2)	12.049(1)
b (Å)	30.267(2)	15.252(1)	12.274(1)
<i>c</i> (Å)	12.376(1)	16.642(1)	19.040(2)
α (°)	90	90	98.20(1)
β (°)	90	107.46(1)	101.54(1)
γ (°)	90	90	112.39(1)
V (Å ³)	12480(2)	3700.0(7)	2475.4(4)
Space group	Fdd2	$P2_1/c$	ΡĪ
Ζ	16	4	2
D_{calc} (g cm ⁻³)	1.664	1.637	1.696
μ (mm ⁻¹)	4.213	3.572	5.093
Absorption correction	integration	integration	integration
T _{min}	0.4043	0.5936	0.4151
T _{max}	0.6698	0.8478	0.7101
No. of reflection	38620	18348	25981
No. of independent	8393	7792	13220
No. of parameters	361	447	594
R_1/wR_2	0.0347, 0.0766	0.0534, 0.1230	0.0500, 0.1243
Good-of-fit (GoF)	1.108	0.833	0.999

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The intensities for the X-ray determinations were collected on a STOE IPDS automated single crystal diffractometer with MoKa radiation at 200 K. The structures were solved by Patterson methods using shelxs-97 [30]. Subsequent Fourier-difference map analyses yielded the positions of the non-hydrogen atoms. Refinement was performed using SHELXL-97 [30]. Hydrogen atoms were calculated for idealized positions and treated with the 'riding model' option of SHELXL. Crystal data and more details of the data collections

Appendix A. Supplementary data

and refinements are contained in Table 3.

CCDC 846928, 846929 and 846930 contains the supplementary crystallographic data for [ReOCl₂(L^{diethyl})], [ReOCl₂(L^{morph})] 2acetone and [ReN(OReO₃)(PPh₃)(L^{diethyl})]·0.5CH₂Cl₂. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/ retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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