Synthesis and Structural Characterization of Novel Oxorhenium(V) Complexes Containing N-Heterocyclic Carbenes

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Keywords: Carbene ligands / Oxo ligands / Rhenium

Reaction of $[ReOCl_3(PPh_3)_2]$ with 2 equiv. of 1,3-diisopropylimidazol-2-ylidene (*i*Pr-carbene) affords $[ReOCl_3($*i*Pr-carbene$)_2]$ (**1**). When an excess of free carbene is used, the dicationic species $[ReOCl($*i*Pr-carbene$)_4][Cl]_2$ (**2**) is isolated. The cationic dioxorhenium complex $[ReO_2($*i*Pr-carbene$)_4]^+$ has been isolated as its I^- (**3**) and ReO_4^- (**4**) salts by different reactions. Treatment of $[ReO_2I(PPh_3)_2]$ with an excess of 1,3-diisopropylimidazol-2-ylidene yields compound **3** in quantitative yield. The cationic species is also isolated as an ReO_4^- salt from the reaction of $[ReO_2Me(PhCCPh)]$ with 1,3-diisopropylimidazol-2-ylidene. The molecular structures of $[ReOCl_3($*i*Pr-carbene$)_2]$ (**1**) and $[ReO_2($*i*Pr-carbene$)_4][ReO_4]$ (**4**) have been determined by single-crystal X-ray diffraction.

Introduction

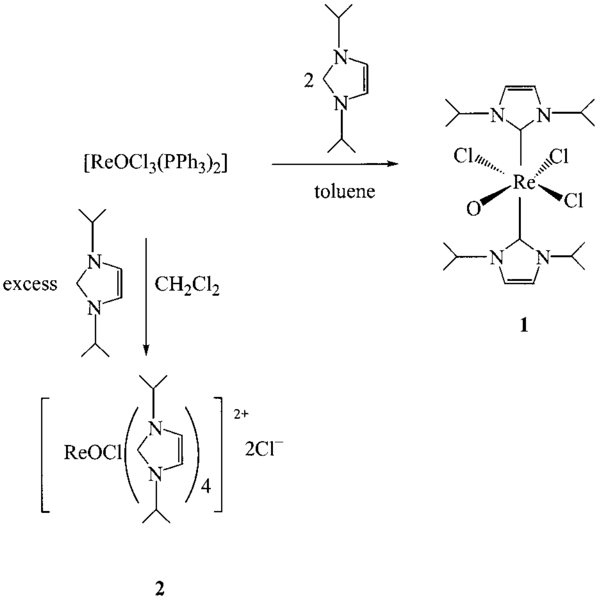
Since the first isolation and X-ray structural characterization of free stable Wanzlick carbenes[1] by Arduengo,[2] a new area of transition metal complexes with these imidazolylidene-type carbenes as ligands has developed.[3]

Acting as strong Lewis bases, N-heterocyclic carbenes (NHC) are promising alternatives for the well-established phosphane ligands in organometallic catalysis. A rich variety of transition metal complexes with this type of ligand is known. However, few examples of oxometal complexes containing N-heterocyclic carbenes have been reported. Indeed, the first example of an oxometal−NHC derivative $[ReO_3Me{\cdot}NHC]$ was published in 1994 by Herrmann et al., although no structural characterization was possible.[5] To the best of our knowledge, the X-ray diffraction studies of $[TiCl_3$(1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene)$(\mu\text{-}O)]_2$,[6] $[VOCl_3$(1,3-dimesitylimidazol-2-ylidene)$]$[7] and $[UO_2Cl_2$(1,3-dimesitylimidazol-2-ylidene)$_2]$[8] are the only examples of oxo transition metal and actinide derivatives containing NHCs that have been reported in the literature. During the preparation of this manuscript the X-ray diffraction studies of the cationic dioxorhenium(V) and -technetium(V) complexes $[ReO_2$(1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene)$_4][PF_6]$ and $[TcO_2$(1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene)$_4][TcO_4]{\cdot}2.5THF$ were reported.[9]

In the present study we describe the synthesis of oxorhenium derivatives containing an NHC ligand and the first X-ray molecular structure of a chlorooxorhenium(V)−NHC complex.

Results and Discussion

Reaction of $[ReOCl_3(PPh_3)_2]$ with 2 equiv. of 1,3-diisopropylimidazol-2-ylidene in toluene at room temperature affords $[ReOCl_3($*i*Pr-carbene$)_2]$ (**1**; *i*Pr-carbene = 1,3-diisopropylimidazol-2-ylidene), which was isolated as a green



Scheme 1. Synthesis of $[ReOCl_3($*i*Pr-carbene$)_2]$ (**1**) and $[ReOCl($*i*Pr-carbene$)_4][Cl]_2$ (**2**)

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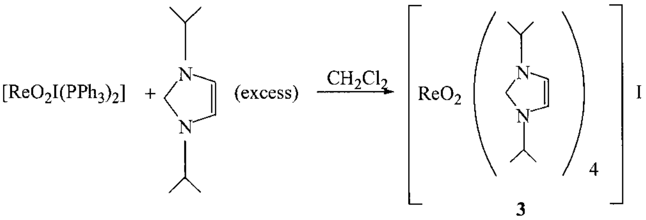
crystalline solid. Double substitution of the triphenylphosphane is preferred since treatment of [$ReOCl_3(PPh_3)_2$] with 1 equiv. of 1,3-diisopropylimidazol-2-ylidene yields a mixture of compound **1** and unchanged starting material. The reaction of [$ReOCl_3(PPh_3)_2$] with an excess of free carbene in dichloromethane gives the green dicationic complex [ReOCl(*i*Pr-carbene)$_4$][Cl]$_2$ (**2**). Compound **2** is the result of the displacement of two chloride ions and both triphenylphosphane ligands by the imidazol-2-ylidene ligand (Scheme 1).

The ^1H NMR spectrum of **1** displays a doublet at δ = 1.40 ppm for the methyl protons of the isopropyl group, a multiplet at δ = 5.75 ppm for the CH proton of the isopropyl group and a singlet at δ = 7.10 ppm for the olefinic protons of the carbene ligand. In contrast, two signal groups of the carbene ligands can be observed for **2**, indicating two inequivalent sets of *i*Pr substituents. This is in agreement with an approximate octahedral environment for the rhenium atom in **2**, with the oxygen and chlorine atoms *trans* to each other. The ^1H NMR spectrum of **2** shows two doublets at δ = 2.63 and 2.94 ppm for the methyl protons of the isopropyl group, two multiplets at δ = 4.92 and 5.35 ppm for the CH proton of the isopropyl group and two multiplets at δ = 8.52 and 8.43 ppm for the olefinic protons of the carbene ligand. The ^{13}C NMR signal of the metal-coordinated carbene C atom is shifted by about 85 ppm to higher field upon complexation of the ligand to the metal atom (δ = 175 ppm for **1** compared with δ = 260 ppm for the free ligand). The IR spectra of **1** and **2** show strong ν(ReO) absorptions at 972 and 989 cm^{-1}, respectively. The mass spectrum of **2** gives the molecular ion *m*/*z* (%) = 423 (100). The main fragment corresponds to the loss of one carbene ligand.

Solid samples of compounds **1** and **2** showed no decomposition in air when exposed for shorts periods of time, but solutions of **1** and **2** are moisture-sensitive; traces of water lead to formation of [ReO_2(*i*Pr-carbene)$_4$][ReO_4].[9] Compound **1** is soluble in aromatic hydrocarbons such as benzene or toluene, while compound **2** is insoluble in toluene, dichloromethane, tetrahydrofuran or diethyl ether, and slightly soluble in acetonitrile.

Crystals of **1** suitable for an X-ray structure analysis were grown from toluene at −20 °C and its molecular structure was determined by single-crystal X-ray diffraction.

The reaction of [$ReO_2I(PPh_3)_2$] with excess of 1,3-diisopropylimidazol-2-ylidene in dichloromethane at −20 °C affords [ReO_2(*i*Pr-carbene)$_4$][I] (**3**) [Equation (1)]. The displacement of the iodine atom and both triphenylphosphane ligands in [$ReO_2I(PPh_3)_2$] by a carbene affords the monocationic species **3**. A similar displacement has been observed previously upon treatment of [$ReO_2I(PPh_3)_2$] with 2 equiv. of dppe yielding [$ReO_2(dppe)_2$][I].[10] Compound **3** was isolated as a brown solid, soluble in dichloromethane and insoluble in hexane or diethyl ether. Its ^1H NMR spectrum shows two resonances for the methyl protons of the isopropyl group, a doublet at δ = 0.70 ppm and a doublet at δ = 1.18 ppm, indicating a hindered rotation of the isopropyl groups, a multiplet for the CH proton of the isopropyl group at δ = 5.74 ppm, and a singlet at δ = 7.09 ppm for the olefinic protons of the carbene. The resonance of the metal-coordinated C atom appears at δ = 172.6 ppm which compares well with other rhenium−carbene complexes such as [Re(1,3-dimethylimidazol-2-ylidene)$_2$I(CO)$_3$] (δ = 175.1 ppm)[11] and [ReO_3Me(1,3-dimethylimidazol-2-ylidene)$_2$] (δ = 176.7 ppm).[5] The mass spectrum of 3^+ gives the molecular ion *m*/*z* (%) = 827 (100). The Re=O vibration of the central dioxorhenium(V) unit appears at 782 cm^{-1}. Similar values have been reported for the Re=O vibration in [ReO_2(1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene)$_4$][PF_6],[9] and in [$ReO_2(dppe)_2$][I].[10]



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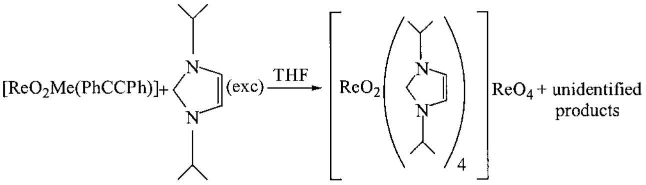
(1)

The [ReO_2(*i*Pr-carbene)$_4$]$^+$ cation is also formed by reaction of [$ReO_2Me(PhCCPh)$] with an excess of 1,3-diisopropylimidazol-2-ylidene in tetrahydrofuran [Equation (2)]. When a solution of [$ReO_2Me(PhCCPh)$] in THF was treated with an excess of 1,3-diisopropylimidazol-2-ylidene, a brown solution was obtained. After removal of the solvent, the residue was extracted into toluene and the solution was cooled to −20 °C. Light-yellow crystals separated from the solution. On the basis of elemental analysis, spectroscopic evidence and X-ray crystallography, the yellow crystals were formulated as [ReO_2(*i*Pr-carbene)$_4$][ReO_4] (**4**). The ^1H NMR spectrum of the toluene-insoluble brown residue shows a mixture of complexes which could not be separated by recrystallisation. It seems reasonable to explain the formation of **4** as the result of the reaction of adventitious water.



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(2)

Crystallographic Studies

A single crystal of the carbene complex **1** was obtained from toluene by standard cooling techniques and its molecular structure was determined by single-crystal X-ray diffraction. Figure 1 shows an ORTEP-style plot of the monomeric neutral molecule. Selected bond lengths and bond angles are reported in Table 1. The asymmetric unit shows two crystallographically independent molecules A and B, each of which is located around a center of inversion, and one solvent molecule (toluene). The intrinsic symmetry of the carbene moiety implies a 50:50 disorder of one chlorine atom and of the oxo ligand. As expected from NMR and IR spectroscopic data, the rhenium atom is coordinated by two carbene ligands in the apical positions of the octahedral coordination sphere. Three chloro and one oxo ligand complete the octahedron in the equatorial plane.

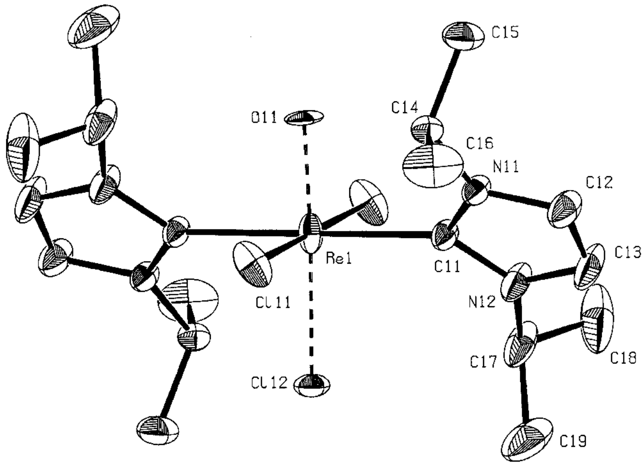

Figure 1. ORTEP representation of compound **1**·toluene (molecule A) in the solid state; thermal ellipsoids are at the 50% probability level; hydrogen atoms are omitted for clarity; dashed lines indicate a disorder (see Exp. Sect.)

Table 1. Selected interatomic distances [Å] and angles [°] for [ReOCl$_3$(*i*Pr-carbene)$_2$(toluene)] (**1**·toluene) and [ReO$_2$(*i*Pr-carbene)$_4$][ReO$_4$] (THF) (**4**·THF)

	1·toluene	**4**·THF
Re1−Cl11	2.3943(12)	
Re1−Cl12	2.298(3)	
Re1−O1/O11	1.770(8)	1.796(4)
Re1−O2		1.798(4)
Re1−C11	2.181(4)	2.185(5)
Re1−C21		2.184(3)
Re1−C31		2.208(5)
Re1−C41		2.207(5)
Cl11−Re1−Cl12	83.83(10)	
Cl11−Re1−O11	90.1(3)	
Cl11−Re1−C11	89.63(11)	
O1−Re1−O2		178.92(15)
C11−Re1−C21		89.9(2)
C11−Re1−C41		89.5(2)
C21−Re1−C31		89.9(2)
C31−Re1−C41		90.7(2)

All bond lengths and bond angles of the N-heterocyclic carbene ligand lie within the typical ranges. The very short Re1−Cl12 distance [2.298(3) Å] and the very long Re1=O11 double bond [1.770(8) Å] in comparison to the statistical range given by the CCDC[12a] are caused by the disorder, and therefore have to be regarded as artificial effects. With 2.3943(12) Å, the Re−Cl11 distance fits the mean value of 2.376[12a] Å very well. The dihedral angles N11−C11−Re1−Cl11 and N11−C11−Re1−O11 are −50.5(4)° and 39.4(5)°, respectively. Thus, the carbene moiety defined by N11−C11−N12 is staggered with respect to the planar ReCl$_3$O unit.

Cooling of a saturated THF solution of **4** to −20 °C for several days yielded clear yellow crystals suitable for X-ray analysis. Figure 2 shows an ORTEP-style plot of the monomeric cationic part of compound **4**. Selected bond lengths and bond angles are reported in Table 1. The asymmetric unit shows one cationic tetrakis(carbene)dioxorhenium moiety, one perrhenate anion, and one solvent molecule (THF). As expected from NMR and IR spectroscopic data, the rhenium atom is coordinated by two oxo ligands in the apical positions and four carbene groups in the basal plane of the octahedral coordination sphere. All bond lengths and bond angles of the N-heterocyclic carbene ligand lie within the typical ranges. The Re1=O11 double-bond lengths [1.796(4) Å and 1.798(4) Å] represent the upper end in the statistical range given by the CCDC.[12b] The dihedral angles N11−C11−Re1−O1, N21−C21−Re1−O1, N31−C31−Re1−O1, and N41−C41−Re1−O1 are 143.6(4)°, 147.5(4)°, 142.0(4)°, and 149.5(5)°, respectively. Thus, the four carbene species are arranged in a propeller mode around the central linear O=Re=O moiety fitting an approximate D_4 symmetry in the solid state.

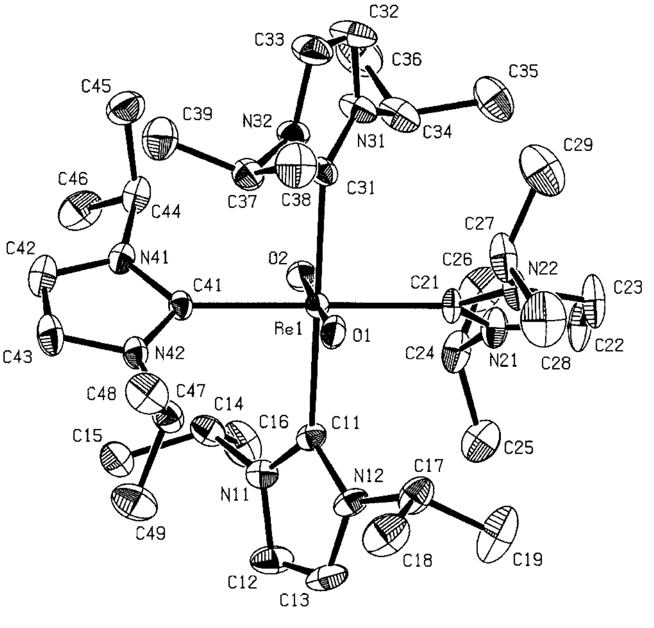

Figure 2. ORTEP representation of the cationic part of compound **4**·THF in the solid state; thermal ellipsoids are at the 50% probability level; hydrogen atoms omitted for clarity

Conclusions

A series of oxorhenium(v) derivatives containing the N-heterocyclic carbene 1,3-diisopropylimidazol-2-ylidene have been prepared. The strong Lewis base carbene easily replaces the triphenylphosphane and halide ligands to give neutral and cationic oxorhenium−carbene complexes.

Experimental Section

General Remarks: All manipulations were carried out under dinitrogen using standard Schlenk-line and glovebox techniques. Solvents were purified by conventional methods and distilled under nitrogen prior to use. NMR spectra were recorded with a Bruker AMX 300 spectrometer. Infrared spectra were recorded with a Unicam Mattson Model 7000 FTIR spectrophotometer using KBr pellets. Electrospray mass spectrometric experiments were performed with a Bruker Daltonic esquire 3000 plus spectrometer. Elemental analyses were performed in our laboratories (ITQB). 1,3-Diisopropylimidazolin-2-ylidene,[13] [$ReOCl_3(PPh_3)_2$],[14] [$ReO_2I(PPh_3)_2$],[15] and [$ReO_2Me(PhCCPh)$][16] were prepared according to literature procedures.

Trichlorobis(1,3-diisopropylimidazol-2-ylidene)oxorhenium(V) (1): 1,3-Diisopropylimidazolin-2-ylidene (4.82 mL of a 0.34 M solution in THF, 1.64 mmol) was added to a suspension of [$ReOCl_3(PPh_3)_2$] (0.68 g, 0.80 mmol) in toluene (0.40 mL) at −20 °C and the reaction mixture was stirred for 30 min. The mixture was then allowed to warm up to room temperature and was stirred for a further 16 h. The toluene solution was filtered and the volume of the filtrate was reduced in vacuo to about 10 mL. Cooling to −20 °C yielded green crystals of **1**. Yield: 0.30 g (65%). $C_{18}H_{32}Cl_3N_4ORe$ (613.05): calcd. C 35.27, H 5.26, N 9.14; found C 35.37, H 5.32, N 9.25. Selected IR data (KBr): ν(ReO) = 972 vs cm^{-1}. ^1H NMR (300 MHz, CD_2Cl_2): δ = 7.10 (s, 2 H, C*H*C*H*), 5.75 (m, 2 H, C*H*Me₂), 1.40 (d, $J_{H,H}$ = 6 Hz, 12 H, CH*Me*) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 174.9 (Re$C_{carbene}$), 119 (*C*H*C*H), 49 (*C*HMe₂), 23 (CH*Me*₂) ppm.

Chlorotetrakis(1,3-diisopropylimidazol-2-ylidene)oxorhenium(V) Dichloride (2): 1,3-Diisopropylimidazolin-2-ylidene (15.23 mL of a 0.34 M solution in THF, 5.18 mmol) was added at −20 °C to a suspension of [$ReOCl_3(PPh_3)_2$] (1 g, 1.29 mmol) in dichloromethane (30 mL). When the addition was completed, the mixture was allowed to warm up to room temperature and was then stirred for a further 20 h. The dichloromethane solution was then filtered, the filtrate was concentrated in vacuo to about 10 mL and was cooled to −20 °C, giving deep-green crystals of **2**. Yield: 0.82 g (72%). $C_{36}H_{64}Cl_3N_8ORe$ (917.53): calcd. C 47.13, H 7.03, N 12.21; found C 46.98, H 6.82, N 12.02. Selected IR data (KBr): ν(ReO) = 989 vs cm^{-1}. ^1H NMR (300 MHz, NCMe): δ = 8.52 (m, 2 H, C*H*C*H*), 8.43 (m, 2 H, C*H*C), 5.35 (q, $J_{H,H}$ = 6 Hz, 2 H, C*H*Me₂), 4.92 (q, $J_{H,H}$ = 6 Hz, 2 H, C*H*Me₂), 2.94 (d, $J_{H,H}$ = 6 Hz, 12 H, CH*Me*₂), 2.63 (d, $J_{H,H}$ = 6 Hz, 12 H, CH*Me*₂) ppm. MS (ES): *m*/*z* (%) = 423/422 (100) [M^+].

Tetrakis(1,3-diisopropylimidazol-2-ylidene)dioxorhenium(V) Iodide (3): 1,3-Diisopropylimidazolin-2-ylidene (14.70 mL of a 0.34 M solution in THF, 5 mmol) was added at room temperature to a solution of [$ReO_2I(PPh_3)_2$] (1 g, 1.14 mmol) in dichloromethane (20 mL). The reaction mixture was stirred for 16 h and was then concentrated in vacuo to about 8 mL. Cooling of the dichloromethane solution to −20 °C afforded the title compound **3**, which was isolated as a brown solid. Yield: 0.84 g (78%). $C_{36}H_{64}IN_8O_2Re$ (954.07): calcd.C 45.32, H 6.76, N 11.74; found C 45.03, H 6.69, N 11.65. Selected IR data (KBr): ν(ReO) = 782 vs cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.09 (s, 2 H, C*H*C*H*), 5.74 (m, 2 H, C*H*Me₂), 1.18 (d, $J_{H,H}$ = 6 Hz, 12 H, CH*Me*₂), 0.70 (d, $J_{H,H}$ = 6 Hz, 12 H, CH*Me*₂) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.6 (Re-$C_{carbene}$), 117.9 (*C*H*C*H), 49.8 (*C*HMe₂), 23.2(CH*Me*₂) ppm.

Tetrakis(1,3-diisopropylimidazol-2-ylidene)dioxorhenium(V) Perrhenate (4): 1,3-Diisopropylimidazolin-2-ylidene (5.5 mL of a 0.14 M solution in THF, 0.77 mmol) was added to a solution of [$ReO_2Me(PhCCPh)$] (0.32 g, 0.77 mmol) in tetrahydrofuran (20 mL) at −30 °C. The mixture was stirred at low temperature for 20 min and at room temperature for 2 h. All the volatiles were removed under vacuum and the residue was extracted into toluene. The volume of the toluene solution was reduced in vacuo to about 10 mL and was kept in a refrigerator at −20 °C to yield the title compound **4** as light-yellow crystals. Yield: 0.28 g (47%). $C_{36}H_{64}N_8O_6Re_2$ (1077.4): calcd. C 40.13, H 5.99, N 10.40; found C 39.89, H 5.86, N 10.35. Selected IR (KBr): ν(ReO) = 910vs cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.09 (s, 2 H, C*H*C*H*), 5.74 (m, 2 H, C*H*Me₂), 1.18 (d, $J_{H,H}$ = 6 Hz, 12 H, CH*Me*₂), 0.70 (d, $J_{H,H}$ = 6 Hz,12 H, CH*Me*₂) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.6 (Re-$C_{carbene}$), 117.9 (*C*H*C*H), 49.8 (*C*HMe₂), 23.2(CH*Me*₂) ppm. MS (ES): *m*/*z* (%) = 827/825 (100) [M^+].

Table 2. Summary of the crystallographic data for [$ReOCl_3$(*i*Pr-carbene)$_2$(toluene)] (**1**·toluene) and [ReO_2(*i*Pr-carbene)$_4$][ReO_4] (THF) (**4**·THF)

	1·toluene	**4**·THF
Empirical formula	$C_{25}H_{40}Cl_3N_4ORe$	$C_{40}H_{72}N_8O_7Re_2$
Formula mass	705.17	1149.48
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$ (no. 14)	Cc (no. 92)
a [Å]	18.7146(2)	16.3702(1)
b [Å]	11.0958(2)	16.2740(1)
c [Å]	14.5390(2)	18.6526(1)
β [°]	102.468(1)	106.0127(3)
V [Å^3]	2947.87(7)	4776.41(5)
Z	4	4
ρ_{calcd} [g·cm^{-3}]	1.589	1.599
μ [mm^{-1}]	4.418	5.116
T [K]	123	153
F(000)	1408	2296
Crystal size [mm]	0.61 × 0.18 × 0.15	0.35 × 0.27 × 0.14
Θ range [°]	2.45/25.35	2.50/25.35
Index ranges $h/k/l$	±22/±13/±17	±19/±19/±22
Reflections collected	66812	48058
Independent reflections [$I_o > 2\sigma(I_o)$/all data/R_{int}]	5391/4598/0.037	8550/8209/0.053
Data/restraints/parameters	5391/0/340	8550/2/531
$R1$ [$I_o > 2\sigma(I_o)$/all data]	0.0325/0.0391	0.0213/0.0235
$wR2$ [$I_o > 2\sigma(I_o)$/all data]	0.0590/0.06615	0.0499/0.0510
GOF	1.136	1.024
Weights a/b	0.0000/12.8838	0.0213/11.5906
$\Delta\rho_{max/min}$ [e·Å^{-3}]	0.87/−0.78	0.69/−0.78

Crystal Structure Determination of 1 and 4: Details of the X-ray experiment, data reduction, and final structure refinement calculations are summarized in Table 2. Crystals of complex **1** (or **4**) suitable for X-ray structure determination were grown from a toluene (THF) solution, fixed with perfluorinated ether in a glass capillary and transferred to the diffractometer. Preliminary examination and data collection were carried out on a Kappa-CCD device (Nonius Mach3) at the window of a rotating anode (Nonius Fr591; 50 kV; 60 mA; 3.0 kW) and graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Data collection was performed at 123 (153) K with an exposure time of 30 (15) s per frame [φ- and ω-scans, rotation modus, $\Delta\varphi/\Delta\omega$ = 2.0° (1.0°)]. A total number of 66812

(48058) reflections were collected.[17a] After merging, a sum of 5391 (8550) independent reflections remained and was used for all calculations. Data were corrected for Lorentz and polarization effects. Corrections for absorption and/or decay effects were applied during the scaling procedure. The unit-cell parameters were obtained by full-matrix least-squares refinements of 5725 (4535) reflections with the program SCALEPACK.[17b] The structures were solved by a combination of direct methods and difference-Fourier syntheses.[17c] All non-hydrogen atoms of the asymmetric unit were refined with anisotropic thermal displacement parameters. All hydrogen atoms were calculated in ideal positions riding on the parent carbon atom. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2 - F_c^2)^2$ with the SHELXL-97 weighting scheme and stopped at a maximum shift/err value < 0.001.[17d] Neutral-atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the International Tables for Crystallography.[17e] All other calculations (including ORTEP graphics) were done with the program PLATON.[17f] Compound **1**·toluene crystallizes with two crystallographically independent molecules A and B in the asymmetric unit. Each of them is located around a center of inversion. This implies a 50:50 disorder of one chlorine ligand and the oxygen atom. Compound **4**·THF appears to be a twin. Twin refinement ends with Flack's parameter at $\varepsilon = 0.443(6)$. Despite the virtual symmetry of the molecule there is no way to transform the coordinates into the centrosymmetric space group *C*2/*c*. Attempts to solve and to refine the experimental data in *C*2/*c* failed. CCDC-229836 (**1**) and -229837 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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[1] [1a] K. Öfele, *J. Organomet. Chem.* **1968**, *12*, 42. [1b] H. W. Wanzlick, H. T. Schönherr, *Angew. Chem. Int. Ed. Engl.* **1968**, *7*, 141.

[2] A. J. Arduengo, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361.

[3] D. Bourissou, O. Guerret, F. P. Gabbaï, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39.

[4] W. A. Herrmann, *Angew. Chem. Int. Ed.* **2002**, *41*, 1290.

[5] W. A. Herrmann, K. Öfele, M. Elison, F. E. Kühn, P. W. Roesky, *J. Organomet. Chem.* **1994**, *480*, C7.

[6] N. Kuhn, T. Kratz, D. Bläser, R. Boese, *Inorg. Chim. Acta* **1995**, *238*, 179.

[7] C. D. Abernethy, G. M. Codd, M. D. Spicer, M. K. Taylor, *J. Am. Chem. Soc.* **2003**, *125*, 1128.

[8] W. J. Oldham Jr, S. M. Oldham, B. L. Scott, K. D. Abney, W. H. Smith, D. A. Costa, *Chem. Commun.* **2001**, 1384.

[9] H. Braband, T. I. Zahn, U. Abram, *Inorg. Chem.* **2003**, *42*, 6160.

[10] M. Freni, D. Giusto, P. Romiti, G. Minghetti, *Gazz. Chim. Ital.* **1969**, *99*, 286.

[11] D. Mihalios, PhD Thesis, Technische Universität München, **1992**.

[12] [12a] A search for hexacoordinate trichlorooxorhenium compounds gives 45 hits within a range for the Re−Cl bond lengths of 2.315−2.481 Å and for the Re=O double bond of 1.605−1.755 Å. [12b] A search for hexacoordinate *trans*-dioxorhenium compounds gives 54 hits within a range for the Re=O double bonds of 1.729−1807 Å. [12c] The Cambridge Structural Database: a quarter of a million crystal structures and rising: F. H. Allen, *Acta Crystallogr., Sect. B* **2002**, *58*, 380−388. [12d] New Software for searching the Cambridge Structural Database and visualizing crystal structures: I. J. Bruno, J. C. Cole, P. R. Edgington, M. Kessler, C. F. Macrae, P. McCabe, J. Pearson, R. Taylor, *Acta Crystallogr., Sect. B* **2002**, *58*, 389−397.

[13] W. A. Herrmann, C. Köcher, L. J. Gooßen, R. J. Artus, *Chem. Eur. J.* **1996**, *2*, 1627.

[14] N. P. Johnson, C. J. L. Lock, G. Wilkinson, *Inorg. Synth.* **1967**, *9*, 145.

[15] G. F. Ciani, G. D′Alfonso, P. F. Romiti, A. Sironi, M. Freni, *Inorg. Chim. Acta* **1983**, *72*, 29.

[16] J. K. Felixberger, J. G. Kuchler, E. Herdtweck, R. A. Paciello, W. A. Herrmann, *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 946.

[17] [17a] Data Collection Software for Nonius Kappa-CCD Devices, Delft, The Netherlands, **2001**. [17b]Processing of X-ray Diffraction Data Collected in Oscillation Mode: Z. Otwinowski, W. Minor, *Methods Enzymol.* **1996**, *276*, 307. [17c] SIR92: A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, *J. Appl. Cryst.* **1994**, *27*, 435−436. [17d] G. M. Sheldrick, *SHELXL-97*, University of Göttingen, Göttingen, Germany, **1988**. [17e] *International Tables for Crystallography*, vol. C (Ed.: A. C. J. Wilson), Kluwer Academic Publishers, Dordrecht, The Netherlands, **1992**; Tables 6.1.1.4 (pp. 500−502), 4.2.6.8 (pp. 219−222), and 4.2.4.2 (pp. 193−199). [17f] A. L. Speck, *PLATON, A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, **2001**.

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