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Rhenium Complexes with 2-(Diphenylphosphinomethyl)aniline: Formation of a Cyclic, Trinuclear Oxorhenium(V) Core

Jennifer Schroer, Stefan Wagner, and Ulrich Abram*

Institute of Chemistry and Biochemistry, Freie Universität Berlin, Fabeckstrasse 34-36, D-14195 Berlin, Germany

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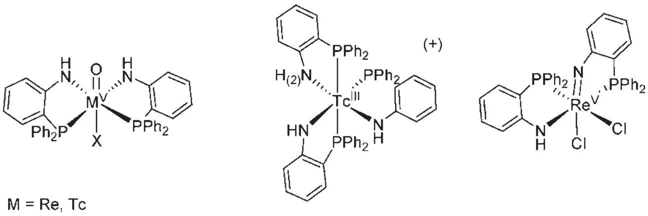
Reactions of 2-(diphenylphosphinomethyl)aniline, H_2L^2, with $(NBu_4)[ReOCl_4]$ yield different oxo rhenium(V) complexes depending on the conditions applied. This comprises monomeric compounds such as $[ReOCl_3(H_2L^2)]$ (**1**), $[ReOCl_2(OMe)(H_2L^2)]$ (**2**), or $[ReO_2(H_2L^2)_2]Cl$ (**5**) as well as the dimeric μ-oxo complex $[\{ReOCl_2(H_2L^2)\}_2O]$ (**3**) and the oxo-bridged trimer $[\{ReOCl(H_2L^2)\}O]_3$ (**4**). The latter compound represents the first example of a hitherto unknown trinuclear, cyclic oxo(V) core. $[\{ReOCl(H_2L^2)\}O]_3$ contains a tensed 6-membered metallacycle, which readily undergoes rearrangements and reactions with additional ligands. Compounds of the compositions **5** and $[ReO_2(H_2L^2)(H_2L^1)]Cl$ (**6**) were isolated either from the decomposition of **4** in CH_2Cl_2/*n*-pentane or from reactions with 2-(diphenylphosphino)aniline, H_2L^1.

Introduction

Phosphines bearing *o*-amino moieties are versatile ligands, which form stable complexes with a variety of transition metals.[1-21] Considerable time was spent on studies with (*o*-aminophenyl) diphenyl phosphine, H_2L^1, which has hard and soft donor atoms and is able to stabilize metals in different oxidation states. The coordination behavior toward Re and Tc has been extensively studied revealing a high flexibility of the ligand.[15-20] Reactions starting from MO_4^- (M = Re, Tc) or other common oxorhenium(V) or oxotechnetium(V) precursors such as $[MOCl_4]^-$ (M = Re, Tc) or $[ReOCl_3(PPh_3)_2]$ give neutral oxo complexes of the composition $[MO(HL^1)_2X]$ (M = Re, Tc; X = halide, hydroxo, alkoxo or carboxylic ligands),[16] neutral or cationic homoleptic $[Tc^{III}(HL^1)_3]$ or $[Tc^{III}(H_2L^1)(HL^1)_2]$ complexes with single-deprotonated amine-phosphines,[19] or even phenylimido species as a result of a complete deprotonation of the amino group and replacement of the oxo ligand,[17,18] depending on the reaction conditions applied (Chart 1).

Chart 1. Selected Rhenium and Technetium Complexes with H_2L^1 [16-19]



M = Re, Tc
X = Cl, Br, OH, OMe, OEt, OPh, OOCMe

As a part of our systematic work in the synthesis of multidentate ligands for rhenium and technetium as foundation for the development of metal-based bioconjugates with the radioactive nuclides ^{99m}Tc, ^{186}Re and ^{188}Re,[22-25] the present

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*To whom correspondence should be addressed. Phone: (#49) 30 83854002. Fax: (#49) 30 83852676. E-mail: abram@chemie.fu-berlin.de.

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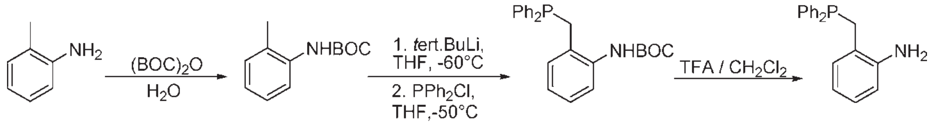
Scheme 1. Synthesis of H_2L^2



H_2L^2

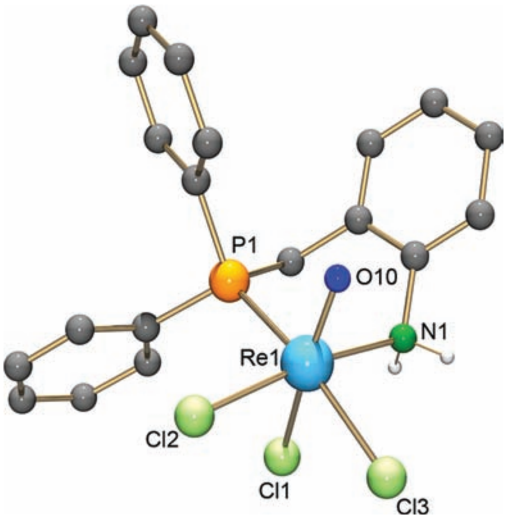


Figure 1. Molecular structure of the complex **1**. Hydrogen atoms at carbon atoms are omitted for clarity.

work describes the synthesis of the novel phosphine amine 2-(diphenylphosphinomethyl)aniline (H_2L^2) and syntheses and structures of several of its oxorhenium(V) complexes. We prepared this phosphine as a building block for the synthesis of ligands with higher denticity, but as foundation for these ongoing studies, knowledge about its basic complex formation behavior is required. With respect to the higher steric flexibility (by insertion of a CH_2 building block) and its expected higher basicity, some differences are expected between the coordination behavior of the diarylalkylphosphine H_2L^2 and the triarylphosphine H_2L^1.

Results and Discussion

Unlike a previous synthesis,[26] H_2L^2 was prepared from *N*-*tert*-butylcarbonate(BOC)-protected *o*-toluidine,[27] by lithiation of the methyl group and subsequent reaction with PPh_2Cl (Scheme 1). After deprotection with trifluoroacetic acid (TFA), the compound H_2L^2 is obtained as a colorless solid in an overall yield of about 60%. The ^{31}P resonance of the phosphine appears at −22.49 ppm. The ^1H NMR spectrum shows a singlet at 2.74 ppm for the methylene group and multiplets for the aromatic protons in the region of 6.51−7.71 ppm. The deprotection of the amino group can clearly be seen in the IR spectrum by the absence of a carbonyl band. Furthermore there are two bands at 3406 and 3330 cm^{-1}, which can be assigned to the NH_2 group. In the ESI^+ mass spectrum of the compound, one peak at m/z = 292 is assigned to $[M + H]^+$. The route used for the synthesis of H_2L^2 can readily be modified and may give access to tri- or tetradentate phosphines with *PNN* or *PNNN* donor sets.

Table 1. Selected Bond Lengths (Å) and Angles (deg) in $[ReOCl_3(H_2L^2)]$ (**1**) and $[ReOCl_2(OMe)(H_2L^2)]$ (**2**)

	1	**2**
Re1−O10	1.672(7)	1.69(2)
Re1−Cl1	2.394(2)	2.468(3)
Re1−Cl2	2.317(3)	2.363(4)
Re1−Cl3/O2	2.451(2)	1.84(2)
Re1−P1	2.440(2)	2.441(3)
Re1−N1	2.173(8)	2.21(2)
P1−Re1−N1	88.0(2)	87.3(3)
O10−Re1−Cl3/O2	164.3(3)	172.2(5)

Hydrogen Bonds in Complex **1**[a]

	d(D−H)	*d*(H···A)	*d*(D···A)	∠ (D−H ··A)
N1−H1A···Cl3#	0.90	2.57	3.354(9)	145.6
N1−H1B···Cl1#	0.90	2.50	3.281(9)	146.1

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

Treatment of $(NBu_4)[ReOCl_4]$ with 1 equiv of H_2L^2 in CH_2Cl_2 or acetonitrile results in the formation of a green solid of the composition $[ReOCl_3(H_2L^2)]$ (**1**). The IR spectrum shows bands at 3224 and 3190 cm^{-1}, which are due to the NH vibrations of the protonated ligand. A very strong band at 987 cm^{-1} is assigned to the Re═O vibration. The structure of **1** is confirmed by X-ray diffraction on green single crystals, which were obtained from overlayering an acetonitrile solution of the complex with toluene. The molecular structure of **1** is shown in Figure 1. Table 1 contains selected bond lengths and angles. The coordination sphere of the Re atom can be best described as a distorted octahedron. The Re═O bond of 1.672(7) Å is in the expected range for a rhenium−oxygen double bond.[28] H_2L^2 coordinates, as expected on the basis of the spectroscopic results, as a bidentate, neutral ligand. The NH hydrogen atoms are involved in hydrogen bonds to the chloro ligands of adjacent molecules. Details are shown in Figure S1b as Supporting Information. The coordination sphere of the rhenium atom in **1** is completed by three chloro ligands. While the Re1−Cl1 and Re1−Cl2 bonds are in the expected range of Re−Cl bonds, the Re1−Cl3 bond of 2.451(2) Å is slightly elongated as a consequence of the structural trans influence of the multiple bonded oxo ligand. The obvious weakening of this bond has consequences for the reactivity of **1**.

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In solution, the complex is not stable, which can be seen from the ^{31}P-{^{1}H} NMR spectra, which are obtained after dissolution of the crystalline compound. They reveal several resonances depending on the solvent used. They all appear in the range between −11.97 and 34.62 ppm and can be assigned to coordinated phosphine. No evidence was found for uncoordinated H_2L^2. Two products of such ongoing reactions in acetonitrile and methanol could be isolated in crystalline form (vide infra), but it is most probable that also the formation of coordination isomers plays a role in such solutions. A similar isomerization was found previously for oxorhenium(V) complexes with H_2L^1.[16] First structural evidence for the nature of the formed complexes after dissolution in methanol was found in the ESI$^+$ MS spectrum of **1**, which was measured in methanol solution. It gives evidence for a species of the composition $[ReOCl(MeO)(H_2L^2)]^+$.

The lability of the chloro ligand trans to the oxo oxygen atom is not surprising and leads to a ready exchange of this ligand. Consequently, the reaction of $(NBu_4)[ReOCl_4]$ with 1 equiv of H_2L^2 in MeOH gives a pale violet precipitate of the composition $[ReOCl_2(OMe)(H_2L^2)]$ (**2**), which can directly be isolated from the reaction mixture. The same compound is obtained when **1** is dissolved in methanol at room temperature. The IR spectrum of **2** reveals NH bands in the range between 3139 and 3286 cm^{-1}, which indicates that the ligand is still protonated. The Re═O vibration is bathochromically shifted by almost 60 cm^{-1} with respect to $[ReOCl_3(H_2L^2)]$ and appears at 929 cm^{-1}. Such a bathochromic shift is consistent with a coordination of a methoxo group trans to the oxo ligand and is a common feature in ReO complexes.[28] An X-ray crystal structure determination confirms the spectroscopic results. The molecular structure of **2** is depicted in Figure 2, and selected bond lengths and angles are compared to the values in **1** in Table 1. While the Re1−O10 bond length remains almost unchanged upon the replacement of Cl$^-$ by MeO$^-$, the Re−O bond to the methanolate ligand is remarkably short, and some double-bond character is indicated also for this bond. Such a situation is not without precedent and has been observed for a number of oxorhenium(V) complexes with other co-ligands.[28] The bonding situation of the chelating aminophosphine remains almost uninfluenced by the Cl$^-$/MeO$^-$ ligand exchange. NMR spectra of **2** of sufficient quality could not be obtained because of the low solubility of this compound in methanol, and rapid ongoing reactions in solvents such as CH_2Cl_2 or acetonitrile.

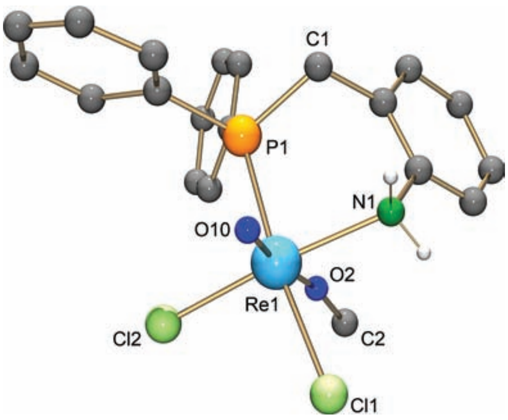
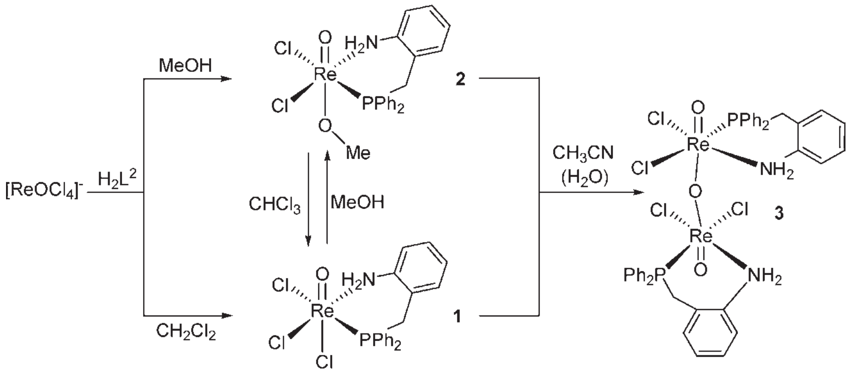


Figure 2. Molecular structure of complex **2**. Hydrogen atoms at carbon atoms are omitted for clarity.

Dissolution of **1** or **2** in acetonitrile results in blue-green solutions, from which turquoise crystals can be isolated after keeping the solutions for 2 weeks at 4 °C. The IR spectrum of this compound contains a strong band at 671 cm^{-1} and a medium band at 975 cm^{-1}, which can be assigned to the Re−O vibration of a μ-oxo dimer and the Re═O vibration.[28] Together with bands at 3278 and 3182 cm^{-1}, which have been assigned to NH vibrations of the non-deprotonated H_2L^2 ligand, the formation of a dimeric compound of the tentative composition $[\{ReOCl_2(H_2L^2)\}_2O]$ (**3**) is strongly suggested (Scheme 2). This is supported by the mass and NMR spectra of the product. The ESI$^+$ MS spectrum contains peaks for the fragments assigned to $[M - Cl]^+$ and $[M - 2Cl + H]^+$. In the ^{31}P-{^{1}H} NMR one peak at −0.35 ppm can be assigned to coordinated phosphorus atoms. The ^{1}H NMR clearly shows two multiplets at 4.75 and 4.96 ppm for the two methylene groups and two multiplets at 8.90 and 9.24 ppm for the amino functions.

An X-ray structure determination confirms the formation of a μ-oxo bridged Re dimer. The compound crystallizes in the triclinic space group $P\bar{1}$ with 2 co-crystallized molecules of acetonitrile per asymmetric unit. The molecular structure is depicted in Figure 3, and selected bond lengths and angles can be found in Table 2. The bond lengths of 1.684(3) Å and 1.699(3) Å for Re1−O10 and Re2−O20 are in the expected range for Re oxo bonds. The monomeric building blocks of the compound can be best described as distorted octahedra with the oxo bridge trans to the terminal oxo ligands. The equatorial positions are occupied each by one H_2L^2 and two chloro ligands. The Re1−O12−Re2 angle of 167.33(13)° significantly deviates from the common linear arrangement

Scheme 2. Reactions of $(NBu_4)[ReOCl_4]$ with H_2L^2 without Addition of a Supporting Base



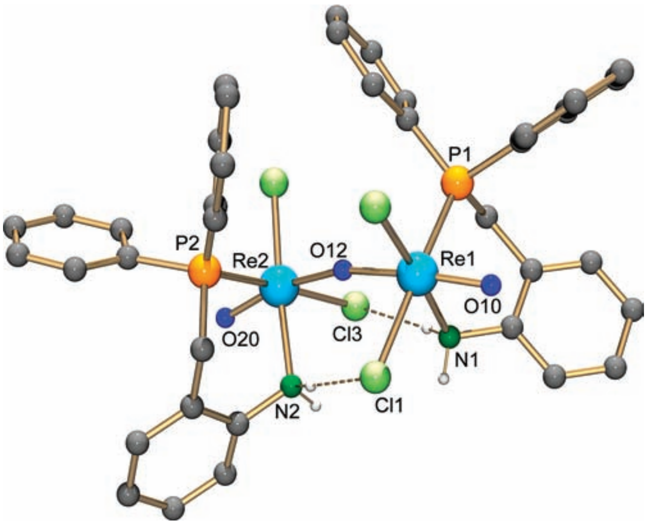


Figure 3. Molecular structure of **3**. Hydrogen atoms at carbon atoms are omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) in [$\{ReOCl_2(H_2L^2)\}_2O$] (**3**)

Re1−O10	1.684(3)	Re2−O20	1.699(3)
Re1−P1	2.424(2)	Re2−P2	2.423(2)
Re1−N1	2.212(4)	Re2−N2	2.214(4)
Re1−Cl1	2.471(2)	Re2−Cl3	2.459(2)
Re1−Cl2	2.349(2)	Re2−Cl4	2.341(2)
Re1−O12	1.936(3)	Re2−O12	1.914(3)
O10−Re1−O12	167.3(2)	O20−Re2−O12	165.8(2)
Re1−O12−Re2	166.4(2)	P1−Re1−N1	87.3(1)
P2−Re2−N2	87.8(1)		

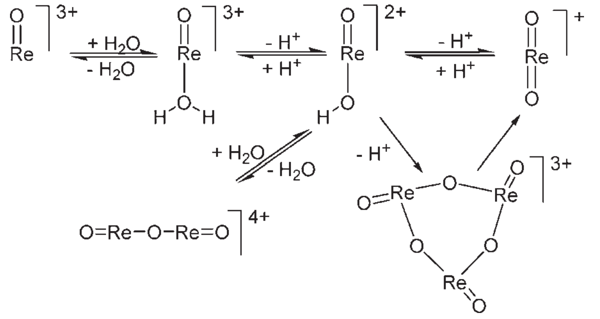
Hydrogen Bonds

	d(D−H)	d(H···A)	d(D···A)	∠ (D−H ··A)
N1−H1A···N99	0.90	2.70	3.384(4)	132.8
N1−H1B···Cl3	0.90	2.35	3.232(4)	168.6
N2−H2A···N99	0.90	2.32	3.141(7)	152.3
N2−H2B···Cl1	0.90	2.33	3.223(4)	171.5

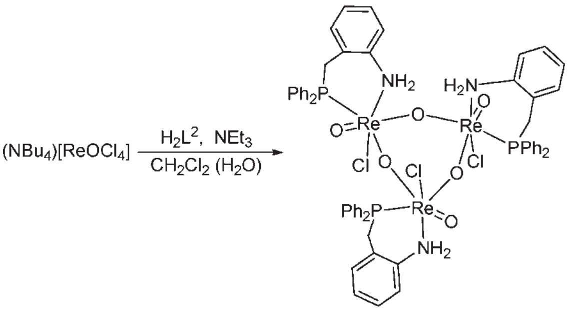
for μ-oxo bridges in Re oxo complexes.[28−30] Such a slightly bent arrangement of the commonly linear {O=Re−O−Re=O}$^{4+}$ core is not without precedent.[31] In the case of complex **3**, it is evident that the distortions are due to hydrogen bonds, which are established between N1 and Cl3 as well as N2 and Cl1. Additional hydrogen bonds are found between the nitrogen atoms of the coordinated H_2L^2 and the solvent acetonitrile (see Figure 3).

The formation of the dimeric, almost linear {O=Re−O−Re=O}$^{4+}$ core results from the replacement of the axial Cl^- ligand in compound **1** by H_2O and subsequent deprotonation of the water ligand. Such a behavior is frequently observed in oxorhenium(V) compounds, and species with {ReO}$^{3+}$, {ReO(OH$_2$)}$^{3+}$, {ReO(OH)}$^{2+}$, and {ReO$_2$}$^{+}$ cores are observed (Scheme 3). Depending on the net charge of the ligands applied, the different central units are formed for optimal charge compensation. Generally, the occupation of the equatorial coordination sphere with neutral ligands will prefer [ReO_2]$^+$ centers (see also the formation of [$ReO_2(H_2L^2)_2$]$^+$ vide infra), whereas ligands with two or more negative charges, will preferably be coordinated to the [ReO]$^{3+}$ core.[28] Consequently in the case of complex **3** (one neutral H_2L^2 ligand, two Cl^-), a central {ReO(OH)}$^{2+}$ unit is preferred, which condenses to the dimeric {O=Re−O−Re=O}$^{4+}$ core. This allows maximum charge compensation by partial transfer of electron density from the terminal oxo ligands to the bridging unit. Commonly (as in the present example) the formation of a central {Re_2O_3}$^{4+}$ unit is irreversible, and only in some exceptional cases has the cleavage of the Re−O−Re backbone of this core been used to prepare monomeric species, as in the synthesis of [$ReO(OEt)Cl_2(py)_2$] from [$Re_2O_3Cl_4(py)_4$].[32]

Scheme 3. Oxorhenium(V) Cores



Scheme 4. Synthesis of the Trimeric Complex [$\{ReOCl(H_2L^2)\}O]_3$ (**4**)



4

The novel amine phosphine H_2L^2 acts in all rhenium(V) complexes described above as a neutral bidentate ligand. This is a clear contrast to the behavior of 2-(diphenylphosphino)-aniline, H_2L^1, which readily deprotonates and forms amido chelates or imido complexes (cf. Chart 1). Even the addition of a supporting base such as NEt_3 does not result in deprotonation of H_2L^2, but in the removal of chloro ligands and the formation of a trimeric compound with a hitherto unprecedented oxorhenium(V) core (Scheme 4).

The reaction of (NBu_4)[$ReOCl_4$] with 1 equiv of H_2L^2 and 3 drops of NEt_3 in CH_2Cl_2 results in the formation of a red compound of the composition [$\{ReOCl(H_2L^2)\}O]_3$ (**4**). Single-crystals of the compound were obtained by careful overlayering of a CH_2Cl_2 solution of the complex with *n*-pentane, and an X-ray structure determination confirms the trimeric structure of the complex. Figure 4a shows the molecular structure of the compound, and Table 3 summarizes selected bond lengths and angles.

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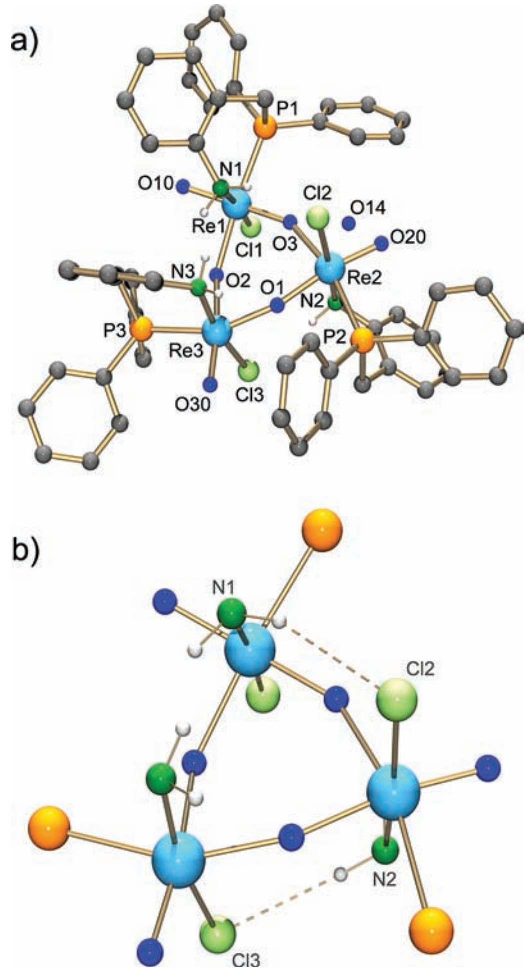


Figure 4. (a) Structure of the complex **4**. Hydrogen atoms are omitted for clarity. (b) Hydrogen bonds, which stabilize the trimeric arrangement.

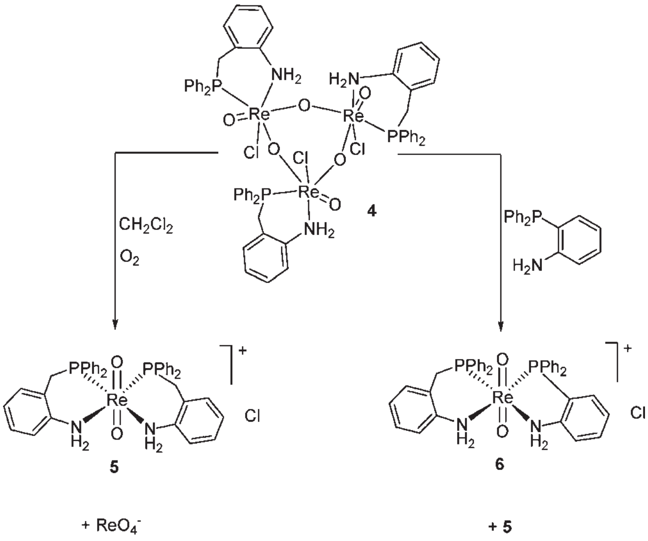
Table 3. Selected Bond Lengths (Å) and Angles (deg) in ReOCl(H_2L^2)}O]$_3$ (**4**)

Re1−O10	1.740(9)	Re1−O3	1.817(8)
Re2−O20	1.700(9)	Re2−O1	1.884(8)
Re3−O30	1.659(8)	Re2−O3	2.050(8)
Re1−O2	2.133(8)	Re3−O1	1.952(8)
Re3−O2	2.107(7)	Re2−O1−Re3	160.1(4)
Re1−O3−Re2	150.7(5)		
Re3−O2−Re1	138.7(4)		

H Bonds	*d*(D−H)	*d*(H···A)	*d*(D···A)	∠ (D−H ··A)
N1−H1D···Cl2	0.90	2.47	3.33(1)	158.7
N2−H2C···Cl3	0.90	2.42	3.32(2)	174.7
N2−H2D···O14	0.90	2.28	3.14(2)	159.8

The monomeric building blocks contain octahedrally coordinated rhenium atoms with the chelate-bonded H_2L^2 and a chloro ligand in cis position to a terminal oxo ligand. The remaining two coordination positions are occupied by the oxo bridges in a way that the oxygen atoms trans to the terminal oxo ligands are bonded trans to the phosphorus atoms of the adjacent unit. This finally gives a trimeric structure which has to the best of our knowledge no precedent in chemistry of group 7 elements. The resulting oxo bridges are bent with angles between 138 and 160°. They are stabilized by hydrogen bonds (Figure 4b), which are established between the nitrogen atoms of H_2L^2 and the chloro ligands of the neighboring unit. Additional hydrogen bonds are formed with solvent water, which co-crystallizes together with CH_2Cl_2 in large channels along the crystallographic *b* axis (see Figure S 4b in Supporting Information).

Scheme 5. Reactions of the Trimeric Complex [{ReOCl(H_2L^2)}O]$_3$ (**4**)



The single crystals of [{ReOCl(H_2L^2)}O]$_3$·2 CH_2Cl_2·2 H_2O are only stable when they are covered with the CH_2Cl_2/pentane mixture from which they are grown. The X-ray structure determination was performed in a capillary, since the single crystals decomposed even at temperatures < −100 °C. Removal of the solvent results in immediate collapse of the single crystals and formation of a reddish powder, which rapidly undergoes an irreversible decomposition under formation of an unattractive, dark oil. This also prevents further spectroscopic characterization.

In the reaction mixture, compound **4** is stable for several hours at room temperature. Prolonged standing, however, results in a color change from red to yellow, and a yellow precipitate is slowly formed. From the IR and NMR spectroscopic analyses of this solid, the formation of [$ReO_2(H_2L^2)_2$]Cl (**5**) is strongly suggested, and was finally confirmed by an X-ray crystal structure determination of the product. Thus, compound **4** undergoes a slow decomposition, from which the dioxo rhenium(V) core results (see also Schemes 3 and 5). Perrhenate is the second product of this decomposition and has been identified in the residue by IR spectroscopy.

Compound **5** can also be prepared directly by treatment of (NBu_4)[$ReOCl_4$] with 2 equiv of H_2L^2 and 3 drops of triethylamine in CH_2Cl_2. Pale yellow crystals deposit from the clear brown reaction solution after reducing the solvent and overlayering with methanol. The IR spectrum reveals a weak band at 3232 cm^{-1}, which can be assigned to the amino function of the ligands. A very strong band at 806 cm^{-1} can be assigned to a $\{ReO_2\}^+$ core.[15] The ^{31}P-{^1H} NMR spectrum of **5** presents a single resonance at 19.91 ppm, which proves the coordination of two equivalent phosphorus atoms. The ^1H NMR spectrum shows two multiplets for the methylene groups at 4.12 and 4.27 ppm, which indicates inequivalence of the protons. Two doublets at 3.15 ppm can clearly be assigned to the NH_2 groups of two coordinated ligands because they disappear after the addition of D_2O. The ESI^+ MS spectrum confirms the existence of a dioxorhenium(V) species with two H_2L^2 ligands with a peak at m/z = 801.18, which corresponds to the complex cation.

Compound **5** crystallizes from a mixture of CH_2Cl_2 and MeOH in the triclinic space group $P\overline{1}$ with two independent $[ReO_2(H_2L^2)_2]^+$ cations, two chloride counterions, and 3/2 methanol molecules per asymmetric unit. The molecular structure of one of the complex cations and the hydrogen bonds, which are established to the corresponding chloride anion, are shown in Figure 5. Selected bond lengths and angles are given in Table 4. The rhenium atom is octahedrally coordinated with two oxo ligands in trans positions to each other. The neutral chelating ligands coordinate in cis arrangement with respect to their nitrogen and phosphorus atoms. The Re═O bonds of the dioxo core of 1.743(5) Å or 1.777(5) Å are slightly longer than those in the corresponding monooxo rhenium(V) complexes **1** and **2**, which is a common feature of oxorhenium complexes and has also been observed in related complexes with the ligand H_2L^1.[15,28] With bond lengths of 2.252(6) Å and 2.241(5) Å, the rhenium−nitrogen bonds can be regarded as single bonds. Hydrogen bonds between the coordinated amine groups and the Cl^- counterions are established in the solid state structure of the compound (Figure 5).

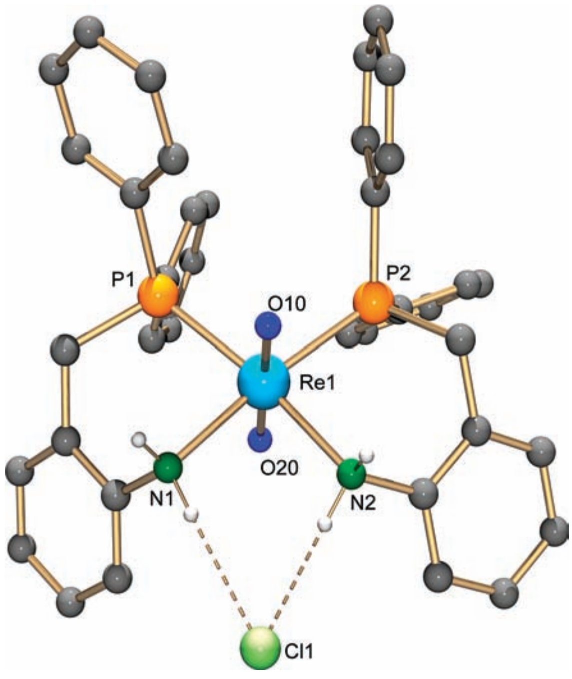


Figure 5. Molecular structure of the complex **5**. Hydrogen atoms at carbon atoms are omitted for clarity.

The inherent instability of the trimeric compound **4**, which finally results in the decomposition described above and the formation of compound **5** and perrhenate, can be applied in the synthesis of mixed-ligand complexes.

This is demonstrated with a reaction that has been performed between **4** and 2-(diphenylphosphino)aniline, H_2L^1. Two compounds, $[ReO_2(H_2L^2)_2]Cl$ (**5**) and $[ReO_2(H_2L^2)(H_2L^1)]Cl$ (**6**), could be isolated from such reactions in crystalline form, but more (non-isolatable) products are contained in the CH_2Cl_2/*n*-pentane reaction mixture as could be seen from the ^{31}P NMR spectrum of the solution, for example, the bis-chelate $[ReOCl(HL^1)_2]$ with two ^{31}P NMR doublets at 18.51 and 6.73 ppm. The reaction mixture also contains considerable amounts of perrhenate, which could be isolated upon concentration as tetrabutylammonium salt.

Compound **5** crystallizes as a CH_2Cl_2 solvate as described above (yield about 5%) and co-crystallized with compound **6** (overall yield 36%). Interestingly, H_2L^1 is not deprotonated in compound **6**. Figure 6 depicts the molecular structure of the mixed-chelate complex **6**, and Table 5 summarizes selected bond lengths and angles of this compound. The values for the co-crystallized complex **5** are given in Table 4 together with those of the methanol solvate.

The Re atom in compound **6** has expectedly a distorted octahedral coordination environment. The axial positions are occupied by the dioxo core, whereas equatorially one

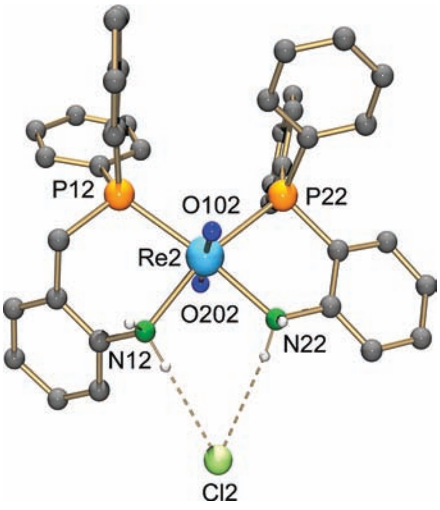


Figure 6. Molecular structure of complex **6**. Hydrogen atoms at carbon atoms are omitted for clarity.

Table 4. Selected Bond Lengths (Å) and Angles (deg) in $[ReO_2(H_2L^2)_2]Cl^a$

Re11−O101	1.743(5)/1.780(5), (1.746(6))	O101−Re11−O201	175.3(2)/175.2(2), (174.9(3))
Re11−O201	1.776(5)/1.745(5), (1.773(6))	P11−Re11−P21	101.52(6)/100.39(6), (100.96(7))
Re11−N11	2.253(6)/2.258(6), (2.239(6))	N11−Re11−N21	85.5(2)/86.0(2), (87.3(3))
Re11−N21	2.239(5)/2.246(5), (2.246(7))	P11−Re11−N11	85.9(2)/85.9(2), (85.7(2))
Re11−P11	2.424(2)/2.414(2), (2.413(2))	P21−Re11−N21	87.0(2)/87.6(2), (86.3(2))
Re11−P21	2.409(29/2.404(2), (2.422(2))		

Hydrogen Bonds[b]

H bonds	*d* (D−H)	*d* (H···A)	*d* (D···A)	∠ (D−H···A)
N11−H11A···Cl11	0.90	2.46/2.46, (2.32)	3.356(6)/3.358(6) (3.201(7))	176.3/177.5, (164.9)
N11−H11B···Cl12	0.90	2.34/2.36, (2.48)	3.227(6)/3.241(6), (3.375(7))	166.7/165.7, (174.5)
N21−H21A···O102	0.90	1.95/1.94, (1.91#)	2.826(7)/2.818(7) (2.791(9)#)	163.9/166.4, (166.4#)
N21−H21B···Cl11	0.90	2.39/2.42, (2.50)	3.246(6)/3.256(6) (3.345(7))	159.4/154.0, (157.1)

[a] The values given are for two crystallograpically independent molecules in $[ReO_2(H_2L^2)_2]Cl$ (**5**) 0.75 MeOH. The values in parentheses refer to the same complex co-crystallized with complex **6**. [b] Symmetry transformations used to generate equivalent atoms: # $-x + 1$, y, z.

Table 5. Selected Bond Lengths (Å) and Angles (deg) in $[ReO_2(H_2L^2)(H_2L^1)]Cl$ (**6**)

Re2−O102	1.775(6)	O102−Re2−O202	176.3(3)
Re2−O202	1.762(6)	P12−Re2−P22	107.71(8)
Re2−N12	2.204(6)	N12−Re2−N22	87.3(2)
Re2−N22	2.245(6)	N12−Re2−P12	80.3(2)
Re2−P12	2.420(2)	N22−Re2−P22	85.0(2)
Re2−P22	2.454(2)		

Hydrogen Bonds[a]

	d(D−H)	d(H···A)	d(D···A)	∠ (D−H···A)
N12−H12A···O201#	0.90	1.87	2.763(9)	172.7
N12−H12B···O201#	0.90	2.63	3.376(7)	141.0
N22−H22C···Cl2#	0.90	2.37	3.268(7)	175.0
N22−H22D···Cl1#	0.90	2.41	3.282(7)	162.0

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

molecule H_2L^1 and one molecule H_2L^2 are coordinated. The phosphorus atoms are arranged in cis position to each other. The Re=O bonds of 1.775(5) Å or 1.762(6) Å are slightly elongated in comparison to the rhenium monooxo core in compound **1**, but are in the normal range for a dioxo core.[16,28] Significant differences are found for the Re−N bonds to the neutral phosphineamine ligands on the cationic mixed-ligand complex under study (2.204(6) for H_2L^2 and 2.245(6) Å for H_2L^1) and the neutral $[ReOCl(HL^1)_2]$ complex (1.990(8) and 2.003(8) Å), which contains two deprotonated chelating ligands.[16] This clearly reflects the protonation/deprotonation pattern in both complexes.

Hydrogen bonds are established between the amino functions and two chloride counterions, as well as to oxo ligands of adjacent complex molecules.

Conclusions

The novel phosphinoaniline H_2L^2 readily forms oxorhenium(V) complexes with different cores. In all cases the ligand remains doubly protonated, which is unexpected with respect to the behavior of (*o*-aminophenyl)diphenylphosphine, H_2L^1, which readily deprotonates during reactions with the same oxorhenium(V) starting material. One of the driving forces for the different reactivity may be the opportunity of a better electron delocalization in the five-membered chelate rings with $\{HL^1\}^-$ compared with the six-membered rings of the H_2L^2 complexes which contain CH_2 units interrupting a possible π-conjugation. Another structure-determining influence might be given by charge compensation and hydrogen bonding, as can be seen by the fully protonated H_2L^1 ligand in the mixed-ligand complex $[ReO_2(H_2L^1)(H_2L^2)]Cl$ (**6**), where the positive charge of the complex is obviously better compensated by hydrogen bonding of the Cl^- counterion than by an oxo/chloro rhenium(V) complex with a deprotonated (*o*-aminophenyl)diphenylphosphine ligand.

Addition of a supporting base to reaction mixtures between H_2L^2 and $(NBu_4)[ReOCl_4]$ does not result in deprotonation of the aminophosphine, but in the formation of a rhenium(V) complex with a hitherto unprecedented trimeric oxorhenium core.

Experimental Section

Materials. All reagents used in this study were reagent grade and used without further purification. Solvents were dried and freshly distilled prior to use unless otherwise stated. $(NBu_4)[ReOCl_4]$ was prepared by a published method.[33] *N*-BOC protected *o*-toluidine was synthesized by a standard procedure.[25]

Physical Measurements. Infrared spectra were measured as KBr pellets on a Shimadzu FTIR-spectrometer between 400 and 4000 cm^{-1}. Electrospray Ionization (ESI) mass spectra were measured with an Agilent 6210 ESI-TOF. All MS results are given in the form: *m*/*z*, assignment. EI mass spectra were recorded with a MAT 711, Varian MAT, Bremen, the electron energy was set to 80 eV. Elemental analysis of carbon, hydrogen, nitrogen, and sulfur were determined using a Heraeus vario EL elemental analyzer. Some values of the elemental analyses of the rhenium complexes significantly differ from the calculated values. This seems to be a systematic problem probably caused by some hydride and/or carbide formation during the combustion process and does not refer to impure samples. Reference samples have been checked by high resolution mass spectrometry. NMR-spectra were taken with a JEOL 400 MHz multinuclear spectrometer.

H_2L^2BOC. *N*-BOC protected *o*-toluidine (5.0 g, 24 mmol) was dissolved in 60 mL of dry tetrahydrofuran (THF) under an atmosphere of argon and cooled to −60 °C. *tert*-Butyllithium (1.5 M, 35 mL, 53 mmol) was added dropwise over a period of 30 min. The reaction mixture was stirred for 3 h and allowed to warm to room temperature. After this time, it was cooled again to −50 °C, and Ph_2PCl (4.0 mL, 22 mmol) was added slowly under stirring. Stirring was continued for 4 h, during which the mixture was slowly warmed to room temperature. After addition of 100 mL of a saturated NaCl solution, the color immediately turned from orange to pale yellow. The organic phase was washed three times with each 50 mL of a NaCl solution and dried over $MgSO_4$. Finally the solvent was removed under vacuum, and the resulting solid was washed with ethanol to yield the product as a colorless precipitate.

Yield: 68% (5.85 g). Anal. Calcd for $C_{24}H_{26}NO_2P$: C, 73.64; H, 6.69; N, 3.57%. Found: C, 73.29; H, 6.38; N, 3.31%. IR (ν in cm^{-1}): 3371 st (N−H), 3070 m (CH_{Ph}), 2977 m ($CH_{methylene}$), 1735 s (C=O). ^1H NMR ($CDCl_3$, δ, ppm): 1.42 (s, 9 H, CH_3), 3.61 (s, 2 H, CH_2), 7.00−7.50 (m, 14 H, Ph). ^{31}P-$\{^1H\}$ NMR ($CDCl_3$, δ, ppm): −18.36, ESI$^+$ MS (*m*/*z*): 392 $[M + H]^+$, 414 $[M + Na]^+$.

H_2L^2. H_2L^2BOC (5.03 g, 12.8 mmol) was dissolved in 20 mL of a 1:1 mixture of CH_2Cl_2/trifluoroacetic acid and stirred for 2 h. After this time, the solution was neutralized with a solution of NaOH. The organic phase was once washed with a solution of NaCl and dried over $MgSO_4$. The solvent was removed under reduced pressure to yield H_2L^2 as a colorless solid, which was stored under nitrogen.

Yield: 85% (3.2 g). Anal. Calcd for $C_{19}H_{18}NP$: C, 78.33; H, 6.23; N, 4.81%. Found: C, 78.29; H, 5.95; N, 4.49%. IR (ν in cm^{-1}): 3406 m (N−H), 3330 m (N−H). ^1H NMR (DMSO, δ, ppm): 2.74 (s, 2 H, CH_2), 6.51−7.71 (m, 14 H, Ph). ^{31}P-$\{^1H\}$ NMR ($CDCl_3$, δ, ppm): −22.49, ESI$^+$ MS (*m*/*z*): 292 $[M + H]^+$.

$[ReOCl_3(H_2L^2)]$ (1). (a) H_2L^2 (29 mg, 0.1 mmol) was added to a solution of $(NBu_4)[ReOCl_4]$ (58 mg, 0.1 mmol) in 3 mL of CH_2Cl_2. The mixture was stirred for 4 h and kept overnight at room temperature. A pale green solid precipitated from the red-brown mother liquor. The product was filtered off and washed with small amounts of CH_2Cl_2. Yield: 48% (29 mg).

(b) $(NBu_4)[ReOCl_4]$ (58 mg, 0.1 mmol) was dissolved in 3 mL of acetonitrile, and H_2L^2 (29 mg, 0.1 mmol) was added together with *p*-toluene sulfonic acid (19 mg, 0.1 mmol), which gave a green solution. The mixture was stirred for 3 h at room temperature. Finally, the mixture was overlayered with toluene and kept quiet for slow diffusion of the solvents. The product was obtained as green crystals. Yield: 42% (25 mg). More product could be recovered as a pale green powder after concentration of the mother liquor.

Elemental analysis: Calcd for $C_{19}H_{18}Cl_3NOReP$: C, 38.04; H, 3.02; N, 2.33%. Found: C, 38.42; H, 2.87; N, 2.38%. IR (ν in cm^{-1}): 3224 m (N−H), 3190 m (N−H), 3124 m (N−H), 987 s (Re=O).

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Table 6. X-ray Structure Data Collection and Refinement Parameters

	[ReOCl$_3$-(H$_2$L^2)]	[ReOCl$_3$(OMe)-(H$_2$L^2)]	[{ReOCl$_2$(H$_2$L^2)}$_2$O]·2 CH$_3$CN	[{ReOCl(H$_2$L^2)-O}$_3$]·2 CH$_2$Cl$_2$·2 H$_2$O	[ReO$_2$(H$_2$L^2)$_2$]-Cl·0.75 MeOH	[ReO$_2$(H$_2$L^2)(H$_2$L^1)]Cl·[ReO$_2$(H$_2$L^2)$_2$]Cl·2.5 CH$_2$Cl$_2$
formula	$C_{19}H_{18}Cl_3$-NOPRe	$C_{20}H_{21}Cl_2$-NO$_2$PRe	$C_{42}H_{42}Cl_4$-N$_4$O$_3$P$_2$Re$_2$	$C_{59}H_{58}Cl_7$-N$_3$O$_8$P$_3$Re$_3$	$C_{38.75}H_{39}Cl$-N$_2$O$_{2.75}$P$_2$Re	$C_{77.5}H_{75}Cl_7$-N$_4$O$_4$P$_4$Re$_2$
M_w	599.86	595.45	1226.94	1836.74	860.31	1870.85
crystal system	triclinic	monoclinic	triclinic	triclinic	triclinic	triclinic
a/ Å	9.448(1)	12.769(2)	11.685(1)	13.532(2)	11.836(1)	15.047(2)
b/ Å	9.913(1)	9.536(1)	13.807(1)	16.606(2)	12.563(1)	15.087(2)
c/ Å	13.075(1)	16.646(2)	14.876(1)	17.555(2)	27.119(2)	20.609(2)
α/ deg	101.64(1)	90	98.07(1)	75.36(1)	93.56(1)	84.05(1)
β/ deg	103.78(1)	92.77(1)	108.25(1)	76.15(1)	95.41(1)	77.87(1)
γ/ deg	114.20(1)	90	91.41(1)	79.55(1)	109.07(1)	61.74(1)
V/ Å^3	1021.0(2)	2024.5(52)	2250.7(3)	3675.0(8)	3775.7(5)	4028.8(9)
space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Z	2	4	2	2	4	2
$D_{calc.}$/g cm^{-3}	1.951	1.954	1.810	1.638	1.513	1.542
μ/mm^{-1}	6.430	6.361	5.724	5.293	3.411	3.362
no. of reflections	11171	10775	25302	21289	40424	34643
no. of independent	5438	4389	12017	15925	20155	17415
no. parameters	236	245	504	791	885	899
R1/wR2	0.0524/0.1491	0.0517/0.1141	0.0308/0.0732	0.0666/0.1554	0.0590/0.1452	0.0594/0.1672
GOF	1.129	0.857	1.055	0.850	0.932	0.961

ESI$^+$ MS (*m*/*z*): 528.03 [M − HCl − Cl]$^+$, 560.06 [M − HCl − Cl + MeOH]$^+$, MS (EI): *m*/*z* 526.7 [M − 2 HCl]$^+$, 562.7 [M − HCl]$^+$.

[ReOCl$_2$(H$_2$L^2)(OMe)] (2). H$_2$L^2 (29 mg, 0.1 mmol) was added to a solution of (NBu$_4$)[ReOCl$_4$] (58 mg, 0.1 mmol) in 7 mL of MeOH and stirred for 4 h at room temperature. Then, the reaction mixture was kept overnight at 4 °C. During this time, pale violet crystals precipitated.

Yield: 54% (32 mg). Elemental analysis: Calcd for $C_{20}H_{19}Cl_2NO_2ReP$: C, 40.34; H, 3.55; N, 2.35%. Found: C, 40.17; H, 3.39; N, 2.27%. IR (*ν* in cm^{-1}): 3286 m (N−H), 3217 m (NH), 3139 m (NH), 929 s (Re=O). MS (EI): *m*/*z* 426.9 [M − HCl, − CH$_3$OH]$^+$, 562.9 [M − CH$_3$OH]$^+$.

[(ReOCl$_2$(H$_2$L^2))$_2$O] (3). [ReOCl$_3$(H$_2$L^2)] (**1**) (45 mg, 0.08 mmol) was dissolved in acetonitrile. The product was obtained as blue crystals upon slow evaporation of the solvent.

Yield: 55% (26 mg). Elemental analysis: Calcd for $C_{38}H_{36}Cl_4N_2O_3Re_2P_2$: C, 39.87; H, 3.17; N, 2.45%. Found: C, 39.96; H, 2.93; N, 2.48%. IR (*ν* in cm^{-1}): 3278 w (N−H), 3182 w (N−H), 975 m (Re=O), 671 vst (Re−O−Re). ^{1}H NMR (CDCl$_3$, *δ*, ppm): 4.75 (m, 2 H, CH$_2$), 4.96 (m, 2H, CH$_2$), 6.99−7.87 (m, 28 H, Ph), 8.90 (d, 2 H, NH$_2$), 9.24 (d, 2 H, NH$_2$) . ^{31}P-{^{1}H} NMR (CDCl$_3$, *δ*, ppm): −0.35. ESI$^+$ MS (*m*/*z*): 1073 [M − 2Cl + H]$^+$, 1109 [M − Cl]$^+$.

[(ReOCl(H$_2$L^2))$_3$O$_3$] (4). A solution of (NBu$_4$)[ReOCl$_4$] (58 mg, 0.1 mmol) and 3 drops of NEt$_3$ were added to H$_2$L^2 (29 mg, 0.1 mmol) in 3 mL of CH$_2$Cl$_2$. The color of the solution immediately turned to red. The mixture was stirred for 15 min at room temperature and then overlayered with *n*-pentane. Red crystals were obtained by slow diffusion of the solvents. The crystals are extremely unstable without the solvent and were prepared for the X-ray measurement at −80 °C with a small amount of solution in a capillary.

Estimated yield: 60%. Elemental analysis as well as more spectroscopic studies could not be performed because of the rapid decomposition of the complex.

[ReO$_2$(H$_2$L^2)$_2$]Cl (5). (a) By decomposition of (**4**): H$_2$L^2 (27 mg, 0.1 mmol) was added to the reaction mixture described above for the synthesis of **4** containing the red crystals of this complex. After standing one day at room temperature, the red crystals disappeared, and yellow (compound **5**) and colorless crystals ((NBu$_4$)Cl) were obtained.

(b) H$_2$L^2 (59 mg, 0.2 mmol) was dissolved in 3 mL of CH$_2$Cl$_2$ and dropwise added to a stirred solution of (NBu$_4$)[ReOCl$_4$] (58 mg, 0.1 mmol) in 2 mL of CH$_2$Cl$_2$. Finally, three drops of triethylamine were added, which resulted in an immediate change of the color to brown. The solution was stirred for 3 h at room temperature, and MeOH (3 mL) was added. Pale yellow crystals appeared during slow evaporation of the solvent. The product was washed with diethylether and dried in air.

Yield: 62% (54 mg). Elemental analysis: Calcd for $C_{38}H_{36}ClN_2O_2ReP_2$: C, 54.57; H, 4.34; N, 3.35%. Found: C, 54.21; H, 3.68; N, 3.07%. IR (*ν* in cm^{-1}): 3232 w (N−H), 806 s (O=Re=O). ^{1}H NMR (DMSO, *δ*, ppm): 3.15 (2d, 4 H, NH$_2$), 4.12 (m, 2H, CH$_2$), 4.27 (m, 2H, CH$_2$), 6.76−7.48 (m, 28 H, Ph). ^{31}P-{^{1}H} NMR (CDCl$_3$, *δ*, ppm): 19.91, ESI$^+$ MS (*m*/*z*): 801 [M − Cl]$^+$.

[ReO$_2$(H$_2$L^2)(H$_2$L^1)]Cl·[ReO$_2$(H$_2$L^2)$_2$]Cl·2.5 CH$_2$Cl$_2$. A solution of (NBu$_4$)[ReOCl$_4$] (58 mg, 0.1 mmol) and 3 drops of NEt$_3$ were added to H$_2$L^2 (29 mg, 0.1 mmol) in 3 mL of CH$_2$Cl$_2$. The mixture was stirred for 15 min at room temperature and then overlayered with *n*-pentane. Red crystals were obtained by slow diffusion of the solvents. H$_2$L^1 (27 mg, 0.1 mmol) was added to this reaction mixture. After 1 day, the red crystals had disappeared, and yellow crystals of [ReO$_2$(H$_2$L^2)(H$_2$L^1)]Cl·[ReO$_2$(H$_2$L^2)$_2$]Cl·2.5 CH$_2$Cl$_2$ deposited at the glass walls.

Estimated yield: about 5 mg (< 10%). ^{31}P-{^{1}H} NMR (CDCl$_3$, *δ*, ppm): −5.50, 0.27, ESI$^+$ MS (*m*/*z*): 787 [ReO$_2$(H$_2$L^2)(H$_2$L^1)]$^+$.

X-ray Crystallography. The intensities for the X-ray determinations were collected on a STOE IPDS 2T instrument with Mo Kα radiation (λ = 0.71073 Å) at 200 K. Standard procedures were applied for data reduction and absorption correction. Structure solution and refinement were performed with SHELXS-97 and SHELXL-97 embedded in the WINGX system.[34,35] Hydrogen atom positions were calculated for idealized positions and treated with the "riding model" option of SHELXL. More details on data collections and structure calculations are contained in Table 6. Ellipsoid plots of all structures are shown in the Supporting Information.

Supporting Information Available: Crystallographic data in CIF format; further details are given in Figures S1−S6 and Tables S1−S6. This material is available free of charge via the Internet at http://pubs.acs.org.

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