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The Formation of Hemiacetal Complexes of Rhenium(V) by Degradation of a Schiff Base

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Dedicated to Professor Bernt Krebs on the Occasion of His 75th Birthday

Keywords: Rhenium; Schiff bases; Hemiacetal; Structure analysis

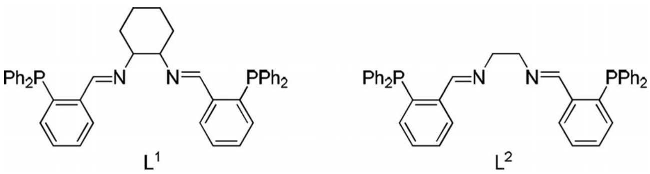
Abstract. Mono- and dinuclear oxidorhenium(V) complexes with hemiacetal ligands were isolated from a reaction of $(NBu_4)[ReOCl_4]$ with a potentially tetradentate Schiff base prepared from (1*R*,2*R*)-cyclohexane-1,2-diamine and (2-formylphenyl)diphenylphosphine in methanol. The hemiacetal is formed by solvolysis of first one imine functionality of the Schiff base, whereas the second remains intact. The resulting amine/iminophosphine coordinates as a tridentate *N*,*N*,*P* ligand in a dinuclear compound. Ongoing degradation of the Schiff base gives more hemiacetal (HL^{1a}) and the final product, the monomeric complex $[ReOCl(L^{1a})_2]$ is formed. Cleavage of the organic framework is not observed during the reaction of $(NBu_4)[ReOCl_4]$ with a related Schiff base derived from ethylene-1,2-diamine and (2-formylphenyl)diphenylphosphine. The Schiff base reacts as a bis-bidentate *N*,*P* ligand and a dinuclear oxorhenium(V) compound with a central ethylene bridge is formed.

Introduction

Schiff bases are versatile ligands, which have played a remarkable role in the exploration of the coordination chemistry of many metals, since they form stable complexes with a large number of metal ions.[1] They can readily be modified by the addition of almost any other donor function. This provides multidentate ligands, which are of interest for bioinorganic research, material science or the development of novel catalysts.[2–4]

Methyltrioxo complexes of rhenium(VII) with various Schiff base ligands as well as oxidorhenium(V) compounds have been studied as potential catalysts for oxidation and epoxidation reactions,[5–8] while several rhenium and technetium Schiff base complexes have been discussed as potential therapeutic or diagnostic radiopharmaceuticals.[9–12] The coordination chemistry of tetradentate Schiff bases has been extensively explored starting from the 1980's. A comprehensive summary of the related work has been given recently.[13] It also contains a detailed discussion about the hydrolytic dimerizations of oxidorhenium(V) complexes, which finally result in the formation of oxido-bridged dimeric (or more rarely) trimeric units. Such reaction patterns, which have been attributed to the conditions during the reactions with the imines, well resembles to the general behavior of oxidorhenium(V) complexes, where μ-oxido compounds are frequently formed when this is favorable for charge compensation.[14]

Relatively less has been reported about solvolysis reactions on the organic skeleton of imine compounds during reactions with rhenium complexes. Exemplarily, two such reactions shall be mentioned herein: (i) the hydrolysis of bis(2-pyridyl)ketone benzoylhydrazone (Hpy_2bhyd) in the presence of $[Re(CO)_3Br_3]^{2-}$ or of the related Re^I complex $[Re(CO)_3Br(Hpy_2bhyd\text{-}py^1,py^2)]$, which both result in the formation of $[Re(CO)_3\{py_2C(OH)O\})]$,[15] and (ii) the degradation of *N*,*N*-dialkylthiocarbamoylbenziminothianes by $[ReOCl_4]^-$, which forms the corresponding benzoylthioureas.[16]



In this paper, we report about reactions of two 2-(benzylimino)phosphines, L^1 and L^2, with $(NBu_4)[ReOCl_4]$.

Results and Discussion

The ligands L^1 and L^2 have been prepared by slightly modified literature procedures from (1*R*,2*R*)-cyclohexane-1,2-diamine or ethylene-1,2-diamine with (2-formylphenyl)diphenylphosphine in toluene and ethanol, respectively. They can be isolated as colorless solids in good yields.[17,18] Both compounds show ^{31}P NMR signals around –13 ppm as is expected

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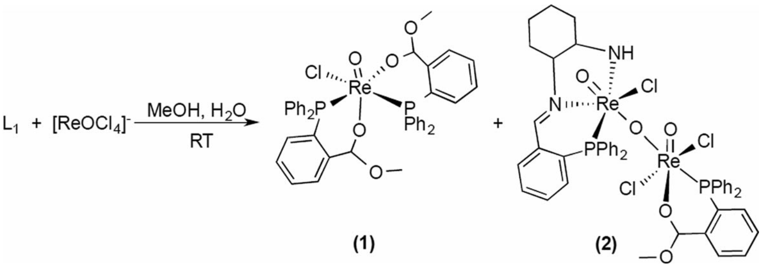


Scheme 1. Reaction of L^1 with $(NBu_4)[ReOCl_4]$.

for phosphines with two magnetically equivalent phosphorus atoms. Intense IR bands at about 1640 cm^{-1} confirm the presence of the imine groups.

Reactions of L^1 with $(NBu_4)[ReOCl_4]$ in acetonitrile or dichloromethane did not give satisfactory products. Such reaction mixtures rapidly changed their colors to deep brown and no solid products could be isolated. ^{31}P NMR spectra of the reaction mixtures show numerous signals, which confirm the presence of various phosphine species (between –10 and –15 ppm) together with signals at lower field, which may be assigned to coordinated phosphines or to phosphine oxides.

Crystalline products could be isolated from reaction mixtures in methanol. Red-brown needle-like crystals of $[ReOCl(L^{1a})_2]$ (**1**) [L^{1a} = $\{Ph_2P(2\text{-}C_6H_4)C(OMe)O\}^-$] are formed in moderate yield together with a small amount (<5%) of orange-red plates of the dinuclear complex $[ReOCl(L^{1b})](\mu\text{-}O)[ReOCl_2(L^{1a})]$ (**2**) [L^{1b} = $H_2N(2\text{-}C_6H_{10})\text{-}N{=}CH(2\text{-}C_6H_4)PPh_2$] (Scheme 1).

The molecular structure of the main product **1** is shown in Figure 1. Selected bond lengths and angles are summarized in Table 1. Compound **1** is a neutral oxidorhenium(V) complex with two unusual chelating *O,P* ligands, which are formed by a metal mediated solvolysis of ligand L^1. The resulting phosphinohemiacetal ligands coordinate as mononegative ligands, one in the equatorial coordination sphere and one with the oxygen atom *trans* to the oxido ligand. The Re–O1 and Re–O3 bond lengths are almost equal, which is surprising with respect to the fact that O3 is situated in *trans* position to the oxido ligand and the expected *trans* influence due to the double bonded oxygen atom. In the present case, however, the Re–O3 bond seems to be rather strengthened than weakened. The transfer of electron density from a Re=O double bond to Re–O bonds in *trans* position is not without precedent and has been observed for a number of (non-chelating) alcoholates before.[14,19] It goes normally along with relatively short Re–O bonds and elongated Re–O–C angles in such molecules. Both effects can also be observed in the present case, where the Re–O3–C37 angle of 146.4(8)° is clearly larger than the Re–O1–C7 one [124.6(7)°]. The values of the O1–C7 and O3–C37 bond lengths together with the corresponding O1–C7–O2 and O3–C37–O4 angles of 108.8(10) and 116.3(16)° confirm the required sp^3 hybridization of the central carbon atoms and the presence of a hemiacetal in favor to an ester group.

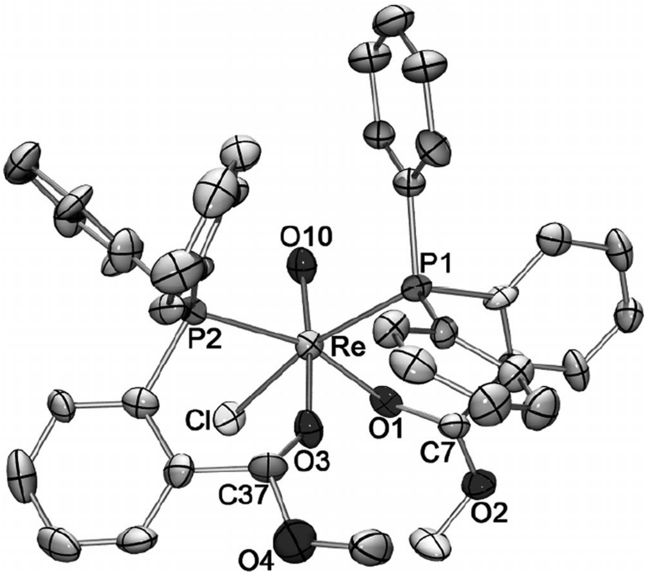


Figure 1. Ellipsoid representation of the molecular structure of **1**. Thermal ellipsoids represent 50 per cent probability.

The latter fact is also supported by the absence of typical ester bands in the IR spectrum of the compound. The Re=O stretch is observed at 984 cm^{-1}. The base peak of the ESI+ mass spectrum of **1** at *m/z* = 881 with the correct isotopic pattern can be assigned to the molecular ion $[M + H]^+$.

Table 1. Selected bond lengths /Å and angles /° in **1**.

Re–O10	1.687(7)	Re–O1	1.981(9)	C7–O2	1.30(2)
Re–Cl	2.415(4)	Re–O3	1.988(7)	O3–C37	1.34(1)
Re–P1	2.474(5)	O1–C7	1.40(1)	C37–O4	1.36(2)
Re–P2	2.470(5)				
O10–Re–P1	89.3(4)	Re–O1–C7	124.6(7)		
O10–Re–P2	90.1(4)	O1–C7–O2	108.8(10)		
O10–Re–Cl	97.8(4)	Re–O3–C37	146.4(8)		
O10–Re–O1	104.3(4)	O3–C37–O4	116.3(16)		
O10–Re–O3	167.9(4)				

The binuclear complex **2** could only be isolated in a small amount as a side product of the above-mentioned reaction. Thus, ongoing spectroscopic measurements could not be performed. Fortunately, the compound appeared in crystalline form and could be studied by X-ray diffraction. Its molecular structure is depicted in Figure 2 and selected bond lengths and angles are given in Table 2.

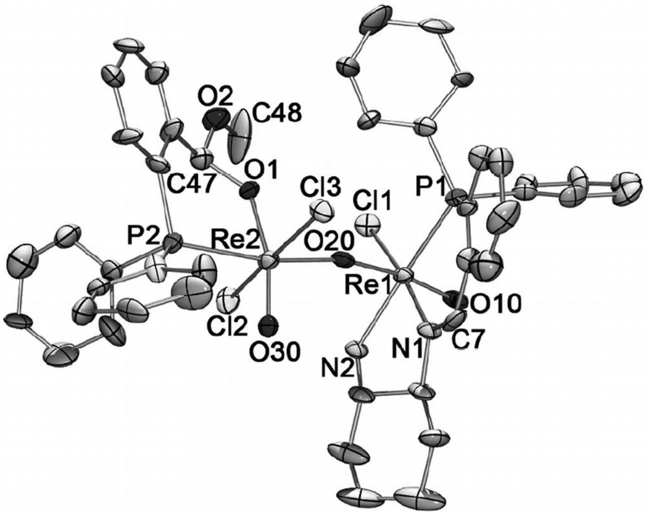


Figure 2. Ellipsoid representation of the molecular structure of **2**. Thermal ellipsoids represent 30 per cent probability.

Table 2. Selected bond lengths /Å and angles /° in **2**.

Re1–O10	1.670(11)	Re2–Cl2	2.431(5)
Re1–Cl1	2.406(5)	Re2–Cl3	2.389(5)
Re1–P1	2.415(4)	Re2–P2	2.456(4)
Re1–N1	2.113(17)	Re2–O1	1.896(11)
Re1–N2	2.191(12)	Re2–O20	2.015(11)
Re1–O20	1.830(12)	O1–C47	1.41(2)
N1–C7	1.26(3)	C47–O2	1.42(2)
Re2–O30	1.676(11)		
O10–Re1–Cl1	92.2(5)	O30–Re2–Cl2	89.9(4)
O10–Re1–P1	95.2(4)	O30–Re2–Cl3	96.2(4)
O10–Re1–N1	88.2(6)	O30–Re2–P2	87.7(4)
O10–Re1–N2	88.2(5)	O30–Re2–O1	165.9(5)
O10–Re1–O20	171.0(5)	O30–Re2–O20	103.1(5)
Re1–N1–C7	130.6(12)	Re2–O1–C47	140.5(10)
Re1–O20–Re2	166.4(6)	O1–C47–O2	112.0(14)

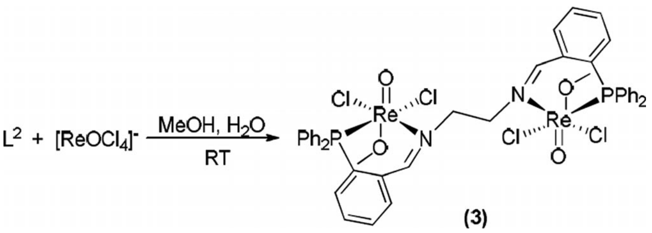
The dimeric compound **2** is composed by two very different oxidorhenium(V) subunits, which are connected by a rare unsymmetric *cis*/*trans* oxido bridge. The equatorial coordination sphere of Re1 is occupied by a tridentate phosphine/imine/amine ligand, which is formed by hydrolysis of L^1, and a chlorido ligand, while two oxido ligands are placed in the axial positions. One of them (O20) acts as bridging ligand to the second unit of the complex. Remarkably, the Re–O distances [1.670(11) and 1.830(12) Å] are similar, which is unusual for oxido-bridged dirhenium complexes and rather remind of dioxidorhenium(V) complexes.[14] This impression is supported by the comparatively long Re2–O20 bond [2.015(11) Å] and the Re1–O20–Re2 angle of 166.4(6)°, which clearly deviates from linearity.

The second subunit of compound **2** contains one chelating phosphine/hemiacetal ligand (as is also coordinated in complex **1**) together with a terminal oxido and two chlorido ligands. The sixth coordination position (in the equatorial coordination sphere of the metal ion) is occupied by the bridging oxygen atom O20. Dimeric μ-oxido complexes of rhenium(V) are not rare,[14] and they are also common in the related chemistry with Schiff base ligands, where they are frequently formed when the synthesis is performed under aerobic conditions and without strict exclusion of moisture.[13] Usually, however, the linear $\{O{=}Re{-}O{-}Re{=}O\}^{4+}$ (*trans, trans*) core is formed with some electron transfer to the oxido bridge. Only some rare cases are known with *cis*,*cis* or *cis*,*trans* coordination of terminal and bridging oxido ligands.[20] In the present case, the common *trans*,*trans* conformation is most probably inhibited by the preferred formation of the building block around the rhenium atom Re2. It contains a stable chelate ring with a tightly bonded hemiacetal oxygen atom in *trans* position of the terminal oxido ligand.

The formation of hemiacetals from solvolysis of coordinated imines is not common and to the best of our knowledge, the present case is the first example with a structural proof. However, similar reactions with coordinated aldehydes or ketones on tricarbonylrhenium(I) centres have been reported previously.[21] $[Re(CO)_3Br(L)]$ complexes (L = pyridine-2-aldehyde or 2-acetylpyridine) readily react with alcohols or amines with formation of hemiacetal or Schiff base complexes. It could be shown that the reactions with the coordinated ketones and aldehydes are orders of magnitudes faster than such between free aldehydes or ketones and aliphatic or aromatic amines.

Also the solvolysis reactions reported herein are clearly metal mediated. This can readily be derived from the fact that the Schiff base L^1 can be recrystallized from alcohols without any evidence of decomposition, Additionally the initial coordination of L^1 is confirmed by the structure of compound **2**, which contains with ligand L^{1b} the first degradation product of L^1. This suggests a mechanism, which involves the formation of an unstable and not isolated complex of the tentative composition of "$[ReO_2(L^1)]^+$". Due to the coordination of the metal, the electrophilicity of the double-bonded carbon atoms is enhanced and they readily undergo stepwise solvolysis with methanol. The released degradation products then form intermediate complexes (such as **2** or the monomeric component complexes of **2**: "$[ReO_2Cl(L^{1b})]$" and "$[ReOCl_2(L^{1a})(solv)]$"), and finally complex **1** with two chelate bonded phosphinohemiacetals. A particular factor in the activation of the electrophilic carbon atom seems to be the steric stress, which is induced by chelating coordination of the Schiff base in five-membered chelate rings or in sterically less flexible tri- or tetradentate ligands.[21] While a high reactivity is observed for the intermediates discussed above, stable Schiff base complexes can be isolated also for tetradentate ligands, when they have a more flexible backbone as *n*-alkyl chains.[13] This hypothesis has also been proven with the *P,N,N,P* Schiff bases under study by the synthesis of ligand L^2, which contains a more flexible ethylene bridge instead of the restricting cyclohexyl residue in L^1.

The reaction of $(NBu_4)[ReOCl_4]$ with L^2 in methanol gives a red solid of $[\{ReOCl_2(OMe)\}_2(\mu\text{-}L^2)]$ (**3**) in medium yield (Scheme 2). There is no evidence of the formation of hemiacetal species in this case. Complex **3** is a centrosymmetric, dimeric compound, in which bidentate coordination of the Schiff base to two central oxidorhenium(V) moieties is observed in favor to the formation of tetradentate coordination.



Scheme 2. Reaction of L^2 with $(NBu_4)[ReOCl_4]$.

The IR spectrum of compound **3** shows the Re=O band at 948 cm^{-1}. The ν(C=N) vibration is observed at 1616 cm^{-1}, which corresponds to a bathochromic shift with respect to the value in the uncoordinated Schiff base. The ^{31}P NMR spectrum of the compound shows a single resonance at δ = 23.2 ppm, which is indicative for a coordinated phosphine. Single crystals of $3\cdot3CH_3NO_2$ were obtained by recrystallization from nitromethane. Figure 3 depicts the molecular structure of the complex. Selected bond lengths and angles are summarized in Table 3.

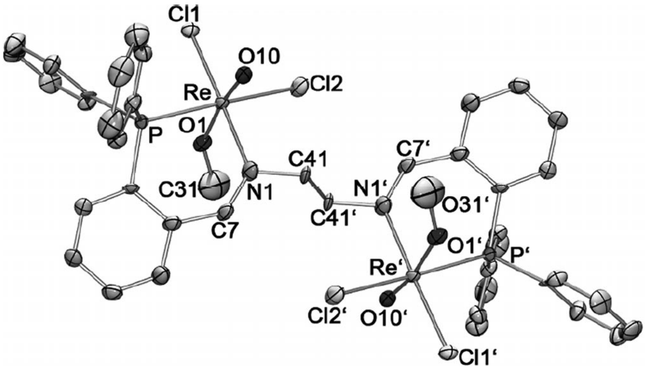


Figure 3. Ellipsoid representation of the molecular structure of **3**. Thermal ellipsoids represent 50 per cent probability.

Table 3. Selected bond lengths /Å and angles /° in $3\cdot3CH_3NO_2$.

Re–O10	1.727(7)	Re–N1	2.162(7)
Re–Cl1	2.363(2)	Re–O1	1.874(6)
Re–Cl2	2.463(2)	N1–C7	1.295(11)
Re–P	2.391(2)	N1–C41	1.490(10)
O10–Re–Cl1	97.2(2)	Re–N1–C7	128.2(6)
O10–Re–Cl2	92.3(2)	Re–N1–C41	117.6(5)
O10–Re–P	92.9(2)	Re–O1–C31	145.9(7)
O10–Re–N1	84.2(3)	C7–N1–C41	114.1(7)
O10–Re–O1	168.2(3)		

The bonding situation inside the dinuclear compound is unexceptional and in accord to previously characterized Schiff base and oxido/methoxido complexes of Re^V.

Conclusions

The imine carbon atoms of a potentially tetradentate Schiff base prepared from (2-formylphenyl)diphenylphosphine and (1*R*,2*R*)-cyclohexane-1,2-diamine are strongly activated by coordination to the oxidorhenium(V) moiety. Reactions with the nucleophile MeOH lead to bond cleavage and formation of a hemiacetal, which finally forms stable complexes of rhenium(V).

Experimental Section

$(NBu_4)[ReOCl_4]$ and (2-formylphenyl)diphenylphosphine were prepared by previously published standard procedures.[17,22]

Infrared spectra were recorded from KBr pellets with a Shimadzu FT instrument in the range 400–4000 cm^{-1}. NMR spectra were recorded with a 400 MHz Jeol spectrometer. The X-ray diffraction data were collected with a STOE IPDS diffractometer with Mo-K_α radiation. The structures were solved by direct methods using SHELXS-97.[23] Subsequent Fourier-difference map analyses yielded the positions of the non-hydrogen atoms. Refinement was performed using SHELXL-97.[23] The positions of hydrogen atoms were calculated for idealized positions and treated with the "riding model" option of SHELXL-97. Crystal data and more details of the data collections and refinements are contained in Table 4.

Synthesis of L^1: (1*R*,2*R*)-Cyclohexane-1,2-diamine (0.19 g, 1.7 mmol) and (2-formylphenyl)diphenylphosphine (1 g, 3.4 mmol) were dissolved in toluene (5 mL) and stirred for 5 h at room temperature. The reaction solution was heated under reflux for 1 h. After removing the solvent, the orange-red residue was recrystallized from MeOH to give a colourless solid. Yield 0.9 g (86 %). **^1H NMR** (400 MHz, $CDCl_3$, ppm): δ = 1.2–1.7 (m, 8 H, CH_2), 3.1 (m, 2 H, N–CH), 6.8–7.7 (m, 28 H, aromatic), 8.68 (d, 2 H, HC=N, J_{PH} = 4.28 Hz). **^{31}P NMR** (400 MHz, $CDCl_3$, ppm): δ = –13.15 ppm. **IR** (KBr): ṽ = 3047 (m), 3004 (w), 2927 (st), 2854 (st), 1635 (st) (C=N), 1581 (w), 1447 (w), 1431 (st), 1369 (m), 1342 (w), 1265 (w), 1203 (w), 1088 (m), 1026 (m), 933 (w), 748 (st), 698 (st), 501 (st) cm^{-1}. **MS** (FAB$^+$): *m*/*z* 659 ($[M + H]^+$, 2 %), 581 ([M – Ph]+, 42 %), 288 ($[M - (PPh_2)_2]^+$, 100 %). Elemental analysis: $C_{44}H_{40}N_2P_2$ (658.75): calcd. C 80.2; H 6.1; N 4.3 %; found: C 80.2; H 6.3; N 4.3 %.

Synthesis of $[ReOCl(L^{1a})_2]$ (1) and $[ReOCl(L^{1b})](\mu\text{-}O)[ReOCl_2(L^{1a})]$ (2): $(NBu_4)[ReOCl_4]$ (58 mg, 0.1 mmol) and L^1 (66 mg, 0.1 mmol) were dissolved in MeOH (5 mL) and stirred at room temperature. After 30 min, a gelatinous deposit was formed, which redissolved in MeOH after a few minutes. A dark solid precipitated after continous stirring for 2 h. It was filtered off and washed with MeOH. Recrystallization of the solid from THF gave red-brown, needle-like crystals of compound **1** (yield: 40 %) together with few orange plates of complex **2**. The lack of sufficient amount of **2** prevented from the characterization of the compound by spectroscopic methods.

Analytical Data for 1: ^1H NMR (400 MHz, $[D_6]$DMSO, ppm): δ = 1.7 (s, 6 H, CH_3), 7.2–8.0 (m, 28 H, aromatic), 10.6 (s, 2 H, CH). **^{31}P NMR** (400 MHz, $[D_6]$DMSO, ppm): δ = 29.9 ppm. **IR** (KBr): ṽ = 3059 (w), 2826 (w), 1481 (w), 1435 (m), 1308 (st), 1242 (st), 1120 (st), 1130 (st), 1099 (st), 1061 (m), 984 (st) (Re=O), 933 (m), 748 (m), 698 (m), 517 (m), 440 (w) cm^{-1}. **MS** (ESI): *m*/*z* 881 ($[M + H]^+$, 100 %). Elemental analysis: $C_{40}H_{36}ClO_5P_2Re$ (880.32): calcd. C 54.6; H 4.1 %; found: C 56.4; H 4.1 %.

Table 4. Crystal data and details of the structure calculations.

	1	2	3·3CH$_3$NO$_2$
Formula	$C_{40}H_{36}ClO_5P_2Re$	$C_{45}H_{45}Cl_3N_2O_5P_2Re_2$	$C_{45}H_{49}Cl_4N_5O_{10}P_2Re_2$
M_w	880.3	1234.5	1396.0
Crystal system	monoclinic	triclinic	triclinic
a /Å	9.832(1)	13.205(5)	9.779(4)
b /Å	18.966(2)	14.613(5)	10.471(5)
c /Å	19.538(2)	17.929(5)	14.896(7)
α /°	90	88.75(1)	106.01(1)
β /°	96.05(1)	75.90(1)	93.80(1)
γ /°	90	72.06(1)	112.48(1)
V /Å^3	3622.9(6)	3187(2)	1329(1)
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
Z	4	2	1
$D_{calcd.}$ /g·cm^{-3}	1.614	1.286	1.744
μ /mm^{-1}	3.56	4.00	4.867
No. of reflections	7598	12196	9721
No. of independent	3040	4809	3796
No. parameters	412	509	303
R_1 / wR_2	0.047/0.097	0.069/0.155	0.044/0.106
GOF	0.677	0.626	1.030

Synthesis of L^2: (2-Formylphenyl)diphenylphosphine (1 g, 3.4 mmol) was dissolved in EtOH (20 mL) and a solution of 1,2-ethylenediamine (0.1 g, 1.7 mmol) in EtOH (10 mL) was added dropwise. The reaction mixture was stirred at room temperature for 1 h and subsequently heated for 3 h. After cooling to room temperature, the product was filtered off and washed with EtOH. Yield 0.85 g (85 %). **^{1}H NMR** (25 °C, [D$_6$]acetone, ppm): δ = 3.5 (s, 4 H, CH$_2$), 6.9 – 7.9 (m, 28 H, aromatic), 8.7 (d, 2 H, HC=N, J_{PH} = 4.52 Hz). **^{31}P{^{1}H} NMR** (25 °C, [D$_6$]acetone, ppm): δ = –13 (s). **^{13}C NMR** (25 °C, [D$_6$]acetone, ppm): δ = 61.9 (CH$_2$), 129.0–140.5 (aromatic), 161.1 (d, C=N, J_{PC} = 75 Hz). **IR** (KBr): ṽ = 3051 (m), 3004 (w), 2920 (m), 2835 (m), 1632 (st) (C=N), 1581 (w), 1477 (m), 1435 (st), 1365 (w), 1277 (w), 1184 (w), 1092 (w), 1064 (w), 1022 (w), 964 (w), 748 (st), 698 (st), 501 (st), 482 (st), 424 (w) cm^{-1}. Elemental analysis: $C_{40}H_{34}N_2P_2$ (604.66): calcd. C 79.5; H 5.7; N 4.6 %; found: C 77.3; H 5.5; N 4.6 %.

Synthesis of [{ReOCl$_2$(OMe)}$_2$(μ-L^2)] (3): (NBu$_4$)[ReOCl$_4$] (58 mg, 0.1 mol) was dissolved in MeOH (5 mL). L^2 (30 mg, 0.05 mmol) was added. The color of the solution turned from green to brownish red. The obtained solid was filtered off and washed with MeOH. Red crystals of **3** were obtained after recrystallization of the product from nitromethane. Yield 40 mg (65 %). **^{1}H NMR** (25 °C, [D$_6$]DMSO, ppm): δ = 3.6 (s, 4 H, CH$_2$), 7.1–8.2 (m, 28 H, aromatic), 8.9 (s, 2 H, HC=N). **^{31}P{^{1}H} NMR** (25 °C, [D$_6$]DMSO, ppm): δ = –1.3 (s). **IR** (KBr): ṽ = 3055 (m), 2959 (st), 2874 (m), 1616 (st), 1562 (w), 1481 (m), 1435 (st), 1308 (w), 1192 (w), 1099 (st), 948 (st) (Re = O), 748 (st), 694 (st), 536 (st), 509 (m) cm^{-1}. Elemental analysis: $C_{42}H_{40}Cl_4N_2O_4P_2Re_2$ (1212.9): calcd. C 41.6; H 3.3; N 2.3 %; found: C 40.2; H 3.2; N 2.5 %.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-957414 (**1**), CCDC-957415 (**2**), and CCDC-957416 (**3**·3CH$_3$NO$_2$) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Acknowledgements

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