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Heterofunctionalized phosphines derived from (2-formylphenyl)diphenylphosphine and their reactions with oxorhenium(V) complexes

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ABSTRACT

Reactions of $[ReOCl_3(PPh_3)_2]$ with a potentially tridentate Schiff base derived from (2-formylphenyl)diphenylphosphine and 2-aminophenol, HL^1P, ($HL^1P = Ph_2PC_6H_4$-2-HC=N(C_6H_4-2-OH)) result in a rapid decomposition of the Schiff base and the formation of a large number of hitherto non-identified metal-containing species, while from similar reactions with the analogoue phosphine oxide HL^1PO, ($HL^1PO = Ph_2P(O)C_6H_4$-2-HC=N(C_6H_4-2-OH)) products of the compositions $[ReOCl_2(PPh_3)(L^1PO)]$ (**1**) and $[Re(NC_6H_4$-2-OH$)Cl_3(PPh_3)_2]$ (**2**) could be isolated. The structure of **2** is an experimental proof of the preceding, metal-induced cleavage of the C–N double bond. A subsequent reaction of the released 2-aminophenol forms the final phenylimido ligand.

Reduction of HL^1P with $NaBH_4$ gives the phosphine amine H_2L^2P ($H_2L^2 = Ph_2P(C_6H_4$-2-$CH_2NH(C_6H_4$-2-OH))) in good yield. Reactions of H_2L^2P with common oxorhenium(V) complexes result in the formation of the stable rhenium(V) complex $[ReOCl_2(HL^2P)]$ (**3**) with a facially coordinated HL^2P^- ligand.

1. Introduction

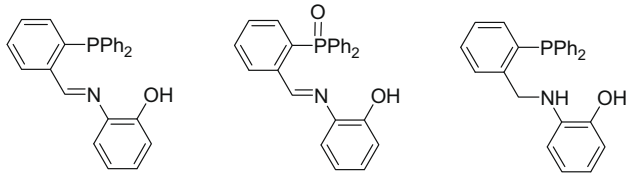
Schiff bases are ligands which play an important role in the coordination chemistry of many transition metals due to the ease of their formation and versatility [1]. Metal complexes of Schiff bases found use in bioinorganic chemistry as models for metal-containing sites in metalloproteins, as catalysts for some organic reactions, or in magneto chemistry [2–6]. They can readily be synthesized by condensation of primary amines with carbonyl components, and this general approach allows access to ligand systems of various denticity. The introduction of additional donor atoms increases the stability of the formed metal complexes and gives the possibility to combine different 'hard' and 'soft' donor atoms in one chelating system, which allows the formation of stable complexes with various metal ions [1].

Rhenium and technetium complexes with such ligands are well-known [7,8], and particularly complexes with tri- and tetradentate Schiff bases found attention in the development of new technetium-based radiopharmaceuticals [9,10]. Despite these well-documented applications, often side reactions, which are mainly related with hydrolysis/solvolysis of the imine bonds, are observed. They frequently decrease the yields and/or result in the formation of unexpected (and undesired) side-products.

Besides these doubtlessly detrimental effects in synthetic chemistry, controlled decomposition of a potential pharmaceutical under certain conditions *in vivo* might be desired in order to control its biological distribution and organ clearance patterns. Thus, it is necessary to characterize the decomposition products and their influence on the course of the complex formation.

Some metal-enhanced hydrolysis has been described for lanthanides [11], but relatively less is known about such reactions of rhenium or technetium complexes. Typically, the electropositive imine carbon atom is the target of a nucleophilic attack by solvent molecules, and in some rare examples metal complexes with fragments of the hydrolyzed Schiff base could be isolated and structurally characterized, e.g. a Re(III) complex with chelate-bonded dehydroacetate, which was formed from a tetradentate N_2O_2 Schiff base [12], or a Re(I) tricarbonyl complex with tripodal coordination of hydroxydi(2-pyridyl)methanolate, which resulted from hydrolysis of a complex with dipyridylketone benzoylhydrazone [13].

Here, we describe reactions of common oxorhenium(V) complexes with two Schiff bases derived from (2-formylphenyl)diphenylphosphine, HL^1P and HL^1PO, as well as with the corresponding phosphine amine H_2L^2P.



HL^1P HL^1PO H_2L^2P

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2. Results and discussion

HL^1P was synthesized adopting a previously published procedure [14]. Some modifications in the experimental conditions, however, increased the yield significantly. The ^{31}P NMR spectrum of the yellow solid shows a resonance at −12.9 ppm. A doublet at 9.1 ppm (J_{PH} = 4.88 Hz) in the ^1H NMR spectrum suggests the presence of the HC=N unit. Oxidation of HL^1P with H_2O_2 in THF results in the formation of HL^1PO in good yields. The ^{31}P NMR signal of the phosphorus atom in the phosphine oxide is found at 31.6 ppm, which corresponds to a low-field shift of 44 ppm compared to the value for HL^1P. The aminophosphine H_2L^2 was prepared by the reduction of HL^1P with an excess of $NaBH_4$ in boiling EtOH. The course of the reaction can readily be tracked by ^1H NMR, where signal of the CH=N protons disappears and a doublet of the methylene protons appears at 4.4 ppm (J_{HH} = 5.24 Hz).

HL^1P reacts with oxorhenium(V) precursors such as $[ReOCl_3(PPh_3)_2]$ or $(NBu_4)[ReOCl_4]$ by almost immediate changes of the colors of the reaction mixtures. However, all our attempts to isolate crystalline products from such mixtures failed. ^{31}P NMR studies of the reaction solutions showed several new signals at negative and positive chemical shift values for each reaction. Number and positions of the signals were strongly dependent on the solvent and the reaction time, which indicates an ongoing decomposition of HL^1P and/or oxidation of the phosphine under formal reduction of the metal ion. The latter type of reaction is not without precedent and has frequently been observed during the interaction of oxorhenium(V) compounds and phosphines, and can principally simply be initiated by released PPh_3 [7]. A detailed analysis of such oxygen transfer reactions has been carried out by Conry and Mayer [15].

In order to simplify the reaction and to minimize the risk of the formation of Re(III) products by a reaction of HL^1P with the oxo oxygen and subsequent formation of HL^1PO in the reaction mixture, we used the phosphine oxide directly. While the course of even this reaction with $(NBu_4)[ReOCl_4]$ remained unclear, HL^1PO reacted within 1 h in boiling THF with the sparingly soluble $[ReOCl_3(PPh_3)_2]$ under formation of a clear green solution. The heating was stopped after 2 h and two crystalline products, the red $[ReOCl_2(PPh_3)(L^1PO–O,N)]$ (**1**) and the green $[Re(NC_6H_4OH)Cl_3(PPh_3)_2]$ (**2**) could be isolated in an approximate ratio of 1:2 (Scheme 1). The amount of compound **2** can be increased by a prolonged reaction time.

The ^{31}P NMR spectrum of **1** exhibits two resonances at 26.8 and 29.4 ppm indicating the presence of L^1PO^- and coordinated PPh_3. The $\nu_{C=N}$ band of the uncoordinated imine compound is bathochromically shifted in the spectrum of the complex and appears at 1566 cm^{-1}. Single crystals of the complex were studied by X-ray diffraction. Fig. 1 shows an ellipsoid representation of **1**. Selected bond lengths and angles are summarized in Table 1. The coordination sphere of the complex is a distorted octahedron with the Schiff base as a singly deprotonated O,N chelate ligand binding via the imine nitrogen and the phenolic oxygen atoms. The oxygen atom O2 is found in *trans* position to the oxo ligand. Such a coordination mode is typical for chelating ligands systems with oxygen donor atoms [7] and goes along with a considerable transfer of electron density from the terminal Re=O bond into the relatively short Re-O2 bond of 1.958(6) Å. The phosphine oxide unit does not contribute to the coordination of the metal atom. This results in a bulky complex molecule, which produces relatively large voids between the molecules, which is also expressed by the relatively low density of the rhenium complex of 1.48 g/cm^3. These holes are almost unoccupied. The highest peaks of electron density located there count approximately 1 $e^-/Å^3$. A refinement with each one water molecule which is disordered in over four positions in such a void improves the *R* value only marginally and is not justified by other experimental data.

The formation of the green phenylimido complex **2** is an unexpected feature of the reaction, but confirms the decomposition of HL^1PO during the reaction with $[ReOCl_3(PPh_3)_2]$. The fact that the amount of **2** formed increases with a prolonged reaction time, also indicates a considerable instability of **1**. The presence of the metal complex is mandatory for the observed ligand decomposition, and all our attempts to decomposed pure HL^1PO in boiling THF failed. The compound resisted such a treatment for 5 h without degradation as has been proven by ^{31}P NMR and TLC experiments. The released 2-aminophenol finally reacts with the oxorhenium core under formation of a phenylimido unit. It is interesting to note that the isolated complex **2** contains two PPh_3 ligands and, consequently, the triphenylphosphine released from $[ReOCl_3(PPh_3)_2]$ is not oxidized immediately by a secondary reaction with the oxo

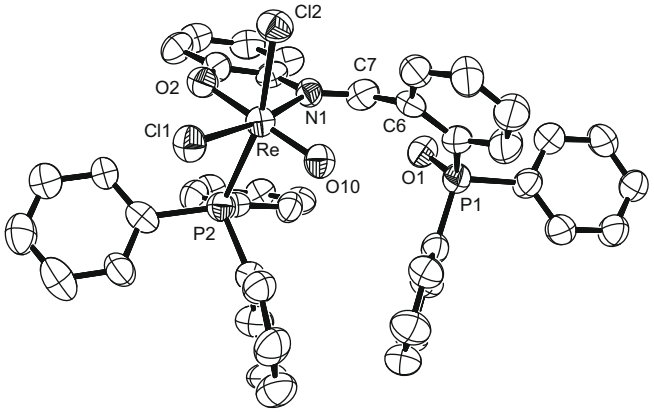
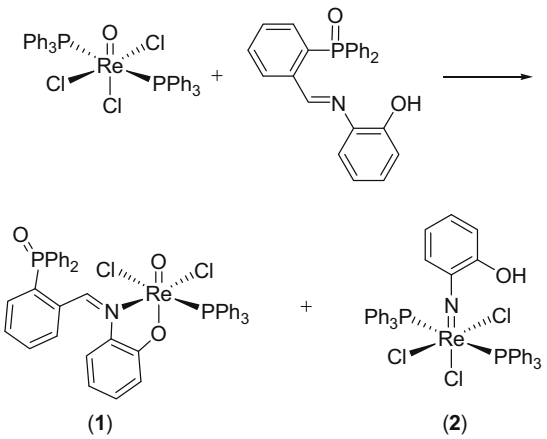


Fig. 1. Ellipsoid representation [21] of $[ReOCl_2(PPh_3)(L^1PO)]$. Thermal ellipsoids represent 50% probability. H atoms have been omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (°) in the $[ReOCl_2(PPh_3)(L^1PO)]$ (**1**).

Re–O10	1.657(6)	Re–O2	1.958(6)
Re–Cl1	2.346(2)	Re–P2	2.469(2)
Re–Cl2	2.386(2)	N1–C7	1.29(1)
Re–N1	2.192(7)	N1–C11	1.44(1)
O10–Re–Cl1	102.4(2)	O10–Re–O2	161.2(3)
O10–Re–Cl2	103.8(3)	N1–Re–O2	76.3(3)
O10–Re–P2	89.7(2)	Re–N1–C7	130.0(6)
O10–Re–N1	87.9(3)		



Scheme 1.

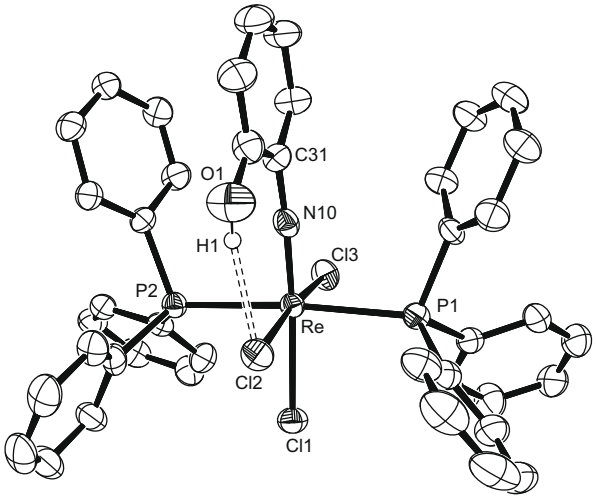
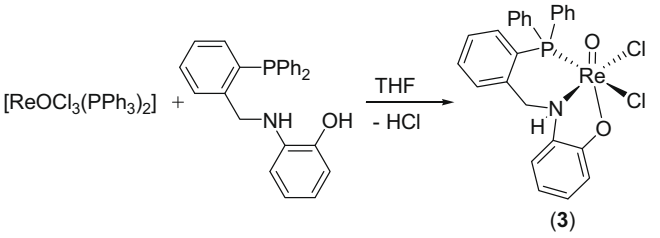


Fig. 2. Ellipsoid representation [21] of $[Re(NC_6H_4OH)Cl_3(PPh_3)_2]$. Thermal ellipsoids represent 50% probability. H atoms (except of H1) have been omitted for clarity.

Table 2
Selected bond lengths (Å) and angles (°) in $[Re(NC_6H_4OH)Cl_3(PPh_3)_2]$.

Re–N10	1.722(6)	Re–P1	2.501(2)
Re–Cl1	2.403(2)	Re–P2	2.490(2)
Re–Cl2	2.425(2)	N10–C31	1.369(9)
Re–Cl3	2.406(2)		
N10–Re–Cl1	173.6(2)	N10–Re–P2	92.1(2)
N10–Re–Cl2	91.3(2)	P1–Re–P2	174.18(5)
N10–Re–Cl3	95.8(2)	Cl2–Re–Cl3	172.92(6)
N10–Re–P1	93.6(2)	Re–N10–C31	174.9(5)



Scheme 2.

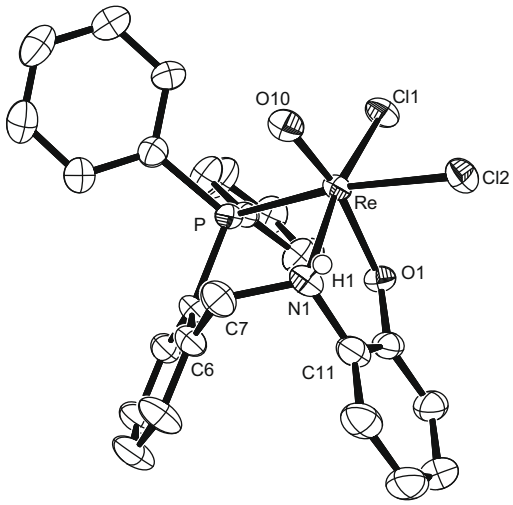


Fig. 3. Ellipsoid representation [21] of *fac*-$[ReOCl_2(HL^2P)]$. Thermal ellipsoids represent 50% probability. H atoms have been omitted for clarity.

Table 3
Selected bond lengths (Å) and angles (°) in *fac*-$[ReOCl_2(HL^2P)]$ (**3**).

Re–O10	1.679(4)	Re–N1	2.195(4)
Re–Cl1	2.344(1)	Re–O1	1.976(3)
Re–Cl2	2.429(1)	N1–C7	1.500(7)
Re–P	2.414(1)	N1–C11	1.469(7)
O10–Re–Cl1	104.1(1)	P–Re–N1	91.0(1)
O10–Re–Cl2	95.7(1)	N1–Re–O1	77.2(2)
O10–Re–P	91.8(1)	Re–N1–C7	115.0(3)
O10–Re–N1	86.4(2)	Re–N1–C11	109.3(3)
O10–Re–O1	163.2(2)	C7–N1–C11	112.1(4)

ligand as has been observed previously, but remains in the solution. This fact is supported by ^{31}P NMR spectra of the reaction mixture. Reactions of anilines with oxo complexes are common and many phenylimido complexes have been prepared in this way, but there are only a few structurally characterized examples of rhenium compounds with (2-hydroxyphenylimido) ligands [16]. Fig. 2 depicts an ellipsoid representation of **2**, selected bond lengths and angles are given in Table 2. Main structural features of the compound are similar to the corresponding 'parent complex' $[Re(NPh)Cl_3(PPh_3)_2]$ [17]. The only remarkable feature in the molecular structure of **2** is an intramolecular hydrogen bond (O1–H1: 0.82 Å, H1–Cl2: 2.25 Å, O1–Cl2: 3.037(7) Å, O1–H1–Cl2: 161.3°), which is established between the phenolic oxygen atom and one of the chloro ligands.

Cleavage of the backbone of the organic ligand is avoided, when the Schiff base is reduced prior reaction with the metal complex. The resulting phosphine amine H_2L^2P is a robust chelating system, which readily reacts with $[ReOCl_3(PPh_3)_2]$ under formation of *fac*-$[ReOCl_2(HL^2P)]$ (**3**) (Scheme 2). The same product is obtained by heating a reaction mixture of H_2L^2P and $(NBu_4)[ReOCl_4]$ in MeOH. The coordination of the phosphorus atom is confirmed by a single resonance in the ^{31}P NMR spectrum at −4.6 ppm, which corresponds to a 12 ppm shift compared to the resonance of uncoordinated H_2L^2P. The IR spectrum contains a medium intense absorption at 968 cm^{-1} related to the Re=O vibration. The broad band at 3452 cm^{-1} is consistent with the stretching vibrations of the NH unit and indicates that the amine donor function is not deprotonated.

The conclusions of the spectroscopic studies are confirmed by an X-ray structure determination of the compound. Fig. 3 depicts the molecular structure of **3** with a facially coordinated HL^2P^- ligand. Expectedly, the oxygen atom occupies the position *trans* to the oxo ligand, and the Re–O1 bond length of 1.973(3) Å is shorter than expected for a rhenium–oxygen single bond. More bond lengths and angles of **3** are summarized in Table 3. The coordination sphere around the metal atom is a distorted octahedron. Main distortions from an ideal octahedron come from the requirements of the four- and five-membered chelate rings, as can clearly be seen at the N1–Re–O1 angle of 77.2°. The Re–Cl2 bond is slightly longer than the Re–Cl1 bond, which is in accord with the stronger structural *trans* influence of the phosphine function compared with the amine.

Concluding it can be stated that a stable tridentate ligand is obtained by the reduction of a Schiff base derived from (2-formylphenyl)diphenylphosphine, while the imine itself undergoes a rapid hydrolysis when reacted with rhenium(V) oxo complexes. This concept can be extended to ligand systems of higher denticity starting from the Schiff bases derived from bis(2-formylphenyl)phenylphosphine or tris(2-formylphenyl)phosphine. Such studies are currently done in our laboratory.

3. Experimental

$(NBu_4)[ReOCl_4]$ [18] and $[ReOCl_3(PPh_3)_2]$ [19] were prepared by literature procedures. IR spectra were measured as KBr pellets on a Shimadzu FTIR-spectrometer 8300. FAB^+ mass spectra were recorded with a TSQ (Finnigan) instrument using a nitrobenzyl alcohol matrix. Elemental analysis of carbon, hydrogen and nitrogen were determined using a Heraeus (vario EL) elemental analyzer. ^1H, ^{13}C and $^{31}P\{^1H\}$ NMR spectra were taken with a JEOL 400 MHz multinuclear spectrometer.

3.1. Synthesis of HL^1P

A mixture of (2-formylphenyl)diphenylphosphine (1.5 g, 5.2 mmol) and 2-aminophenol (0.57 g, 5.2 mmol) were suspended in 10 mL of ethanol and heated under reflux for 1.5 h. The product precipitated as a yellow powder, which was filtered off and washed with cold ethanol. Yield 1.8 g (93%). Elemental *Anal.* Calc. for $C_{25}H_{20}NOP$ (381.13): C, 78.73; H, 5.29; N, 3.67%. Found: C, 78.92; H, 5.29; N, 3.51%. ^1H NMR (400 MHz, DMSO-d_6, ppm): δ 6.72–8.30 (m, 18H, aromatic), 8.78 (s, 1H, OH), 9.14 (d, 1H, HC=N, J_{PH} = 4.88 Hz). ^{13}C NMR (DMSO-d_6, ppm): δ 115–136 (aromatic), 156 (HC=N). ^{31}P NMR (DMSO-d_6, ppm): δ −12.9 s. IR (KBr, cm^{-1}): 3283 (st), 3043 (m), 3013 (w), 2881 (w), 1632 (st), 1581 (m), 1481 (st), 1431 (m), 1369 (w), 1281 (w), 1250 (st), 1270 (m), 1122 (w), 1026 (w), 968 (w), 883 (w), 856 (w), 744 (st), 698 (st), 602 (w), 509 (m), 482 (m). MS (EI): *m/z* 381 ($[M]^+$, 83%), 304 ($[M-Ph]^+$, 100%).

3.2. Synthesis of HL^1PO

HL^1P (1 g, 2.6 mmol) was dissolved in 5 mL of THF and H_2O_2 (0.3 mL, 30% wt.) was added. After stirring the reaction mixture for 10 min, 10 mL brine solution was added. The organic phase was separated and dried over $MgSO_4$. HL^1PO was isolated as an analytically pure, yellow powder after removal of the solvent. Yield 0.98 g (95%). Elemental *Anal.* Calc. for $C_{25}H_{20}NO_2P$ (397.41): C, 75.56; H, 5.07; N, 3.52%. Found: C, 75.68; H, 5.05; N, 3.61%. ^1H NMR (400 MHz, DMSO-d_6, ppm): δ 6.55–8.30 (m, 18H, aromatic), 8.9 (s, 1H, HC=N), 10.05 (s, 1H, OH). ^{31}P NMR (DMSO-d_6, ppm): δ 31.6 s. ^{13}C NMR (DMSO-d_6, ppm): δ 164.1 (s, HC=N). IR (KBr, cm^{-1}): 3420 (w), 3058 (m), 3024 (m), 1632 (m), 1578 (m), 1485 (s), 1435 (m), 1377 (w), 1354 (w), 1292 (m), 1223 (m), 1257 (st), 1157 (m), 1130 (m), 1111 (m), 1072 (m), 1029 (w), 968 (w), 767 (m), 748 (st), 702 (s), 578 (m), 540 (st).

3.3. Synthesis of H_2L^2

HL^1P (1.4 g, 3.6 mmol) and $NaBH_4$ (0.91 g, 24 mmol) were suspended in 20 mL of EtOH and heated for 10 min. After the reaction solution became colorless, the solvent was removed under vacuum and the product was extracted with 15 mL of Et_2O. The organic phase was washed with water and dried over $MgSO_4$. A colorless solid was obtained after removing the solvent under vacuum. Yield 1.2 g (88%). Elemental *Anal.* Calc. for $C_{25}H_{22}NOP$ (383.4): C, 78.31; H, 5.78; N, 3.65%. Found: C, 77.05; H, 5.42; N, 3.14%. ^1H NMR (400 MHz, DMSO-d_6, ppm): δ 4.36 (d, 2H, CH_2, J_{HH} = 5.24 Hz), 5.4 (t, 1H, NH J_{HH} = 5.84 Hz), 6.05–7.6 (m, 18H, aromatic), 9.2 (s, 1H, OH). ^{31}P NMR (DMSO-d_6, ppm): δ −16.6. IR (KBr, cm^{-1}): 3514 (w), 3425 (m), 3055 (m), 2866 (w), 1604 (st), 1515 (st), 1438 (m), 1242 (m), 1192 (m), 1041 (w), 737 (st), 698 (m).

3.4. Synthesis of $[ReOCl(PPh_3)(L^1PO)]$ (**1**) and $[Re(NC_6H_4OH)Cl_3(PPh_3)_2]$ (**2**)

$[ReOCl_3(PPh_3)_2]$ (0.17 g, 0.2 mmol) and HL^1PO (79 mg, 0.2 mmol) were dissolved in 20 mL of THF and heated under reflux for 2 h. The volume of the solution was reduced to 3 mL and cooled to −10 °C. Two different types of crystalline products, red **1** and green **2**, deposited and were separated mechanically. Overall yield of both compounds: 74 mg (ca. 80%). After a reaction time of 2 h an approximate ratio of 1:2 between the compounds **1** and **2** was obtained. The relative amount of **2** increased with prolonged reaction times.

3.4.1. Data for **1**

Elemental *Anal.* Calc. for $C_{43}H_{34}Cl_2NO_3P_2Re$ (1·THF) (931.7): C, 55.43; H, 3.68; N, 1.50%. Found: C, 53.87; H, 3.66; N, 1.62%. ^1H NMR (400 MHz, DMSO-d_6, ppm): δ 6.85–8.04 (m, 38H, aromatic), 10.58 (s, 1H, HC=N). ^{31}P NMR (DMSO-d_6, ppm): δ 26.08 (s, PPh_3), 29.44 (s, $OPPh_3$). IR (KBr, cm^{-1}): 3055 (m), 2851 (w), 1697 (w), 1589 (w), 1566 (w), 1477 (m), 1431 (st), 1194 (m), 1161 (m), 1095 (m), 1068 (w), 1026 (w), 941 (w), 748 (st), 694 (st), 517 (st). MS (FAB^+): *m/z* 896 ($[M-Cl]^+$, 1%), 635 ($[M-C_{18}H_{14}PCl]^+$, 3%).

3.4.2. Data for **2** · *THF*

Elemental *Anal.* Calc. for $C_{42}H_{35}Cl_3NOP_2Re$ (924.2): C, 54.58; H, 3.82; N, 1.52%. Found: C, 55.18; H, 4.19; N, 1.27%. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 6.17−7.87 (m, 34H, aromatic). ^{13}C NMR ($CDCl_3$, ppm): δ 127.8–138.7 (aromatic). ^{31}P NMR ($CDCl_3$, ppm): δ −20.68 s. IR (KBr, cm^{-1}): 3132 (w), 3055 (w), 2970 (w), 2851 (w), 1593 (w), 1473 (m), 1431 (m), 1342 (w), 1238 (w), 1200 (m), 1153 (w), 1092 (m), 1061 (w), 1030 (w), 999 (w), 744 (m), 694 (st), 652 (w), 517 (st).

3.5. Synthesis of fac-$[ReOCl_2(HL^2P)]$ (**3**)

$[ReOCl_3(PPh_3)_2]$ (83 mg, 0.1 mmol) was dissolved in 20 mL of THF and H_2L^2P (38 mg, 0.1 mmol) was added as solid. The mixture was stirred under reflux for 1 h, whereupon an olive-green suspension was obtained. The solvent was removed under reduced pressure and the residue was suspended in 5 mL of MeOH. The olive-green solid was filtered through a Celite pad and washed twice with MeOH. Recrystallization from CH_2Cl_2/MeOH gave green plates. Yield: 46 mg (71%). Elemental *Anal.* Calc. for $C_{25}H_{21}NO_2Cl_2PRe$ (656.5): C, 45.74; H, 3.38; N, 2.13%. Found: C,

Table 4
X-ray structure data collection and refinement parameters.

	1	**2** · THF	**3** · MeOH
Formula	$C_{43}H_{34}Cl_2NO_3P_2Re$	$C_{46}H_{43}Cl_3NO_2P_2Re$	$C_{26}H_{23}Cl_2NO_3PRe$
M_w	931.75	996.37	687.54
Crystal system	monoclinic	triclinic	triclinic
a (Å)	9.5913(7)	10.874(1)	9.496(1)
b (Å)	14.0170(7)	12.198(1)	10.733(1)
c (Å)	31.379(3)	16.772(1)	13.209(1)
α (°)	90	73.12(1)	81.49(1)
β (°)	97.62(1)	75.09(1)	78.66(1)
γ (°)	90	82.03(1)	74.98(1)
V (Å^3)	4181.4(5)	2052.4(2)	1268.1(2)
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
Z	4	2	2
D_c (g cm^{-3})	1.480	1.612	1.801
μ (mm^{-1})	3.148	3.274	5.094
Absorption correction	integration	integration	integration
T_{min}/T_{max}	0.8554/0.7745	0.8172/0.6807	0.5527/0.4470
Number of reflections	24050	20987	14474
Number of independent	8732	10926	6753
Number parameters	470	543	294
R_1/wR_2	0.0608/0.1200	0.0547/0.1203	0.0381/0.1951
Goodness of fit	0.919	1.022	1.053
Deposit umber (ccdc)	715062	715063	715064

45.91; H, 3.34; N, 1.91%. ^{1}H NMR (400 MHz, DMS-d_6, ppm): δ 5.0 (d, 1H, CH_2, J_{HH} = 11 Hz), 5.6 (d, 1H, CH_2, J_{HH} = 11 Hz), 6.0 (t, 1H, NH), 6.3–7.8 (m, 18H, aromatic). ^{31}P NMR (DMSO-d_6, ppm): δ −4.6. IR (KBr, cm^{-1}): 3452 (m), 3058 (m), 2943 (w), 2846 (w), 1485 (st), 1435 (m), 1257 (m), 188 (w), 1099 (w), 968 (m), 771 (m), 752 (m), 694 (m), 633 (m), 517 (m). MS (FAB$^+$): 654.9 ([M]$^+$, 7%), 620 ([M−Cl]$^+$, 48%).

3.6. X-ray structure determinations

The intensities for the X-ray determinations were collected on a STOE IPDS with Mo Kα radiation. The structures were solved by direct methods using SHELXS-86 [20] or SHELXS-97 [20]. Subsequent Fourier-difference map analyses yielded the positions of the non-hydrogen atoms. Refinement was performed using SHELXL-97 [20]. Hydrogen atom positions were calculated for idealized positions and treated with the 'riding model' option of SHELXL. Crystal data and more details of the data collections and refinements are contained in Table 4.

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Appendix A. Supplementary data

Supplementary crystallographic 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. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2009.01.016.

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