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p-Tolylimido rhenium(V) complexes with phenolate-based ligands: synthesis, X-ray studies and catalytic activity in oxidation with *tert*-butylhydroperoxide †

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<Abstract> The reactions of *mer*-[Re(*p*-NTol)$X_3(PPh_3)_2$] (X = Cl, Br) with chelating phenolate-based ligands (2-(2-hydroxy-5-methylphenyl)benzotriazole (HL^1), 2-(2-hydroxyphenyl)benzothiazole (HL^2) or 2-(2-hydroxyphenyl)benzoxazole (HL^3)) afforded a series of *p*-tolylimido rhenium(V) complexes *cis*- or *trans* -(X,X)-[Re(*p*-NTol)X_2(L)(PPh_3)]·*y*MeCN (where X = Cl, Br; L = L^1, L^2, L^3 and y = 0–2) and [Re(*p*-NTol)X(L)$(PPh_3)_2$]Z·*p*PPh_3 (where X = ReO_4, PF_6; L = L^1, L^2, L^3 and p = 0 or 1). The reported compounds were characterized by elemental analysis FT-IR, NMR (^{1}H, ^{13}C and ^{31}P) and X-ray crystallography. Interestingly, halide ions of [Re(*p*-NTol)$Cl_2(L^1)(PPh_3)$]·MeCN (**1**) and [Re(*p*-NTol)$Cl_2(L^2)(PPh_3)$]·2MeCN (**3**) are in *cis* relative

dispositions, whereas the complexes [Re(*p*-NTol)Br_2(L)(PPh_3)] (L^1 for **2**, L^2 for **4** and L^3 for **6**) and [Re(*p*-NTol)Cl_2(L^3)(PPh_3)] (**5**) were found to be *trans*-(X,X) isomers. The compounds [Re(*p*-NTol)X(L)$(PPh_3)_2$](PF_6) (X = Cl, Br; L = L^1 and L^2) and [Re(*p*-NTol)X(L^3)$(PPh_3)_2$](PF_6)·PPh_3 (X = Cl, Br) have been tested in oxidative catalysis. A few compounds exhibited very good catalytic properties in oxidation of alcohols with *tert*-BuOOH (TBHP) in acetonitrile solution at moderate temperatures. Complex [Re(*p*-NTol)Cl(L^2)$(PPh_3)_2$]PF_6 (**13**) is the catalyst of choice for oxidation of 1-phenylethanol to acetophenone (in 80% yield; turnover number attained 290 after 30 h) and cyclooctanol to cyclooctanone (in 88% yield). Noteciably lower activity has been found in the oxidation of alkanes with TBHP. Product distribution in the oxidation of methylcyclohexane indicates some sterical hindrance around the reaction center.

1. Introduction

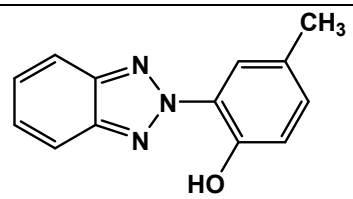
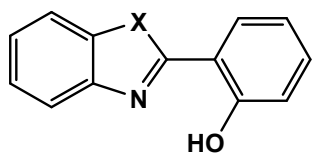
The chemistry of transition metal complexes containing multiple bonds to nitrogen atoms is currently the subject of intensive research. Such complexes have been successfully employed in the nitrogen fixation,[1] catalytic hydroamination of alkynes,[2] hydrosilylation of ketones and aldehydes,[3] synthesis of various nitrogen heterocycles,[4] activation of hydrocarbons including methane [5] and in cycloaddition reactions with unsaturated organic substrates.[6]

Reported by Chatt and Rowe in 1962, first Re arylimido complexes [$ReCl_3$(NAr)$(PPh_3)_2$] were obtained in the reactions of [$ReOCl_3(PPh_3)_2$] and aniline as the source of the imido ligand.[7] Since then, many other valuable synthetic methodologies to imido rhenium complexes have been developed, including the reactions of oxo complexes with isocyanates ArNCO,[8] phosphinimines RN=PPh (R=alkyl or aryl),[9] arylazopyridines YC_6H_4-N=NC_5H_4N (Y = H, 3-Me, 4-Me, 4-C1),[10] silylamines $RN(SiMe_3)_2$,[11] hydrazines [12] as well as alkylation or arylation of nitrido complexes,[13] thermolysis of alkyliminoalkyl metal complexes [14] and the homolytic cleavage and addition of azo compounds.[15] The synthesis of imido complexes directly from perrhenate is an essential step for any complexes to have viability as radiopharmaceuticals, as the emitting radionuclides ^{186}Re (1.07 MeV β-emitter, $t_{1/2}$ = 90h) and ^{188}Re (2.12 MeV β-emitter, $t_{1/2}$ = 17 h) are isolated as perrhenate ion from a ^{188}W generator system.[16] Another convenient synthetic strategy for making imido complexes of rhenium concerns ligand exchange reactions with retention of the imido moiety.[17]

Our recent research has demonstrated that compounds [Re(*p*-NTol)$X_3(PPh_3)_2$] (X = Cl, Br) are versatile starting materials in the synthesis of Re imido complexes incorporating uninegative N,O-donor ligands.[18] The studies revealed that the geometry of the resulted [Re(*p*-NTol)X_2(L)(PPh_3)] (HL = pyridine-2-carboxylic acid, pyrazine-2-carboxylic acid, indazole-3-carboxylic acid and quinoline-2-carboxylic acid) complexes may be tuned by careful selection of chelating carboxylate-based ligands (steric and electronic properties) as well as experimental conditions. What is more, the results confirmed

that different regio-isomers might have a significant influence on catalyst activity. The complexes [Re(*p*-NTol)X_2(pyz-2-COO)(PPh_3)] and [Re(*p*-NTol)X_2(ind-3-COO)(PPh_3)] have been found to catalyze oxidation of alkanes with H_2O_2 and *tert*-butyl hydroperoxide (TBHP) and of alcohols with TBHP,[18a] whereas the catalytic activity of [Re(*p*-NTol)X_2(py-2-COO)(PPh_3)] was demonstrated in the synthesis of *N*-substituted ethyl glycine esters from ethyl diazoacetate and amines.[18b]

To obtain other catalytically active imido rhenium compounds and get a deeper understanding of the isomeric preferences in the group of [Re(*p*-NTol)X_2(L)(PPh_3)] we decided to carry out more in-depth investigations of imido rhenium complexes [Re(*p*-NTol)X_2(L)(PPh_3)] incorporating phenolate-based chelating ligands: 2-(2-hydroxy-5-methylphenyl)benzotriazole (HL^1), 2-(2-hydroxyphenyl)benzothiazole (HL^2), 2-(2-hydroxyphenyl)benzoxazole (HL^3) (Scheme 1).

	
HL^1	HL^2 for X = S; HL^3 for X = O

Scheme 1 Phenolate-based ligands employed in this study.

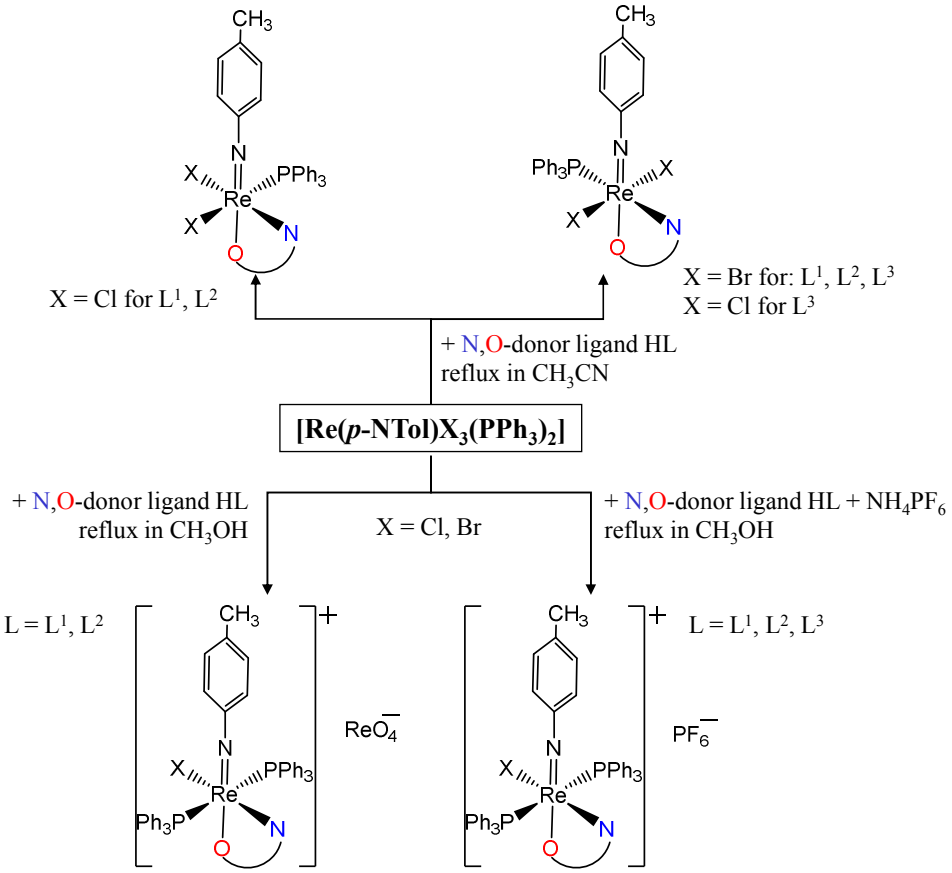
X-Ray structure of *cis*-(Cl,Cl)-[Re(*p*-NTol)Cl_2(L^1)(PPh_3)]·MeCN (**1**) was reported in the previous paper.[18d] The present contribution covers the synthesis, X-Ray structure and spectroscopy of the following new imido complexes: *trans*-(Br,Br)-[Re(*p*-NTol)Br_2(L)(PPh_3)] (L^1 for **2**, L^2 for **4** and L^3 for **6**), *cis*-(Cl,Cl)-[Re(*p*-NTol)Cl_2(L^2)(PPh_3)]·2MeCN (**3**) and *trans*-(Cl,Cl)-[Re(*p*-NTol)Cl_2(L^3)(PPh_3)] (**5**), [Re(*p*-NTol)Cl(L)$(PPh_3)_2$]ReO_4 (L^1 for **7** and L^2 for **9**), [Re(*p*-NTol)Br(L^1)$(PPh_3)_2$]ReO_4 (**8**), [Re(*p*-NTol)Br(L^2)$(PPh_3)_2$]ReO_4·PPh_3 (**10**), [Re(*p*-NTol)Cl(L)$(PPh_3)_2$]PF_6 (L^1 for **11** and L^2 for **13**), [Re(*p*-NTol)Br(L)$(PPh_3)_2$]PF_6 (L^1 for **12** and L^2 for **14**) and [Re(*p*-NTol)X(L^3)$(PPh_3)_2$]PF_6·PPh_3 (Cl for **15** and Br for **16**).

2. Results and discussion

2.1 Synthesis of the complexes

The complexes *cis*- or *trans*-(X,X)-[Re(*p*-NTol)X_2(L)(PPh_3)]•*y*MeCN (where X = Cl, Br; L = L^1, L^2, L^3 and *y* = 0–2) and [Re(*p*-NTol)X(L)$(PPh_3)_2$]Z•*p*PPh_3 (where X = Cl, Br; Z = ReO_4, PF_6; L = L^1, L^2, L^3 and *p* = 0 or 1) were prepared by reacting of *mer*-[Re(*p*-NTol)$X_3$$(PPh_3)_2$] (X= Cl, Br) and 2-(2-hydroxy-

5-methylphenyl)benzotriazole (HL^1), 2-(2-hydroxyphenyl)benzothiazole (HL^2) or 2-(2-hydroxyphenyl)benzoxazole (HL^3). The synthetic strategy of **1**–**16** is presented in Scheme 2.



Scheme 2 Formation of complexes **1**–**16**.

As shown in Scheme 2, the solvent seems to play a crucial role in the determination of activation energetics and reaction kinetics and thermodynamics, and thus the resultant structures of imido Re complexes incorporating L^1, L^2 and L^3 ligands.

The reactions between *mer*-[Re(*p*-NTol)X_3(PPh_3)$_2$] and 2-(2-hydroxy-5-methylphenyl)benzotriazole (HL^1), 2-(2-hydroxyphenyl)benzothiazole (HL^2) or 2-(2-hydroxyphenyl)benzoxazole (HL^3) in acetonitrile resulted in the formation of monosubstituted compounds of formula [Re(*p*-NTol)X_2(L)(PPh_3)].

Interestingly, the halide ions of [Re(*p*-NTol)Cl_2(L^1)(PPh_3)]·MeCN (**1**) and [Re(*p*-NTol)Cl_2(L^2)(PPh_3)]·2MeCN (**3**) are arranged in *cis* geometry, whereas X^- ligands of [Re(*p*-NTol)Br_2(L)(PPh_3)] (L^1 for **2**, L^2 for **4** and L^3 for **6**) and [Re(*p*-NTol)Cl_2(L^3)(PPh_3)] (**5**) occupy *trans* positions to each other. The *trans*-*cis* rearrangement must take place during the chelation step, no *cis*-*trans* isomerism in solution was evidenced by NMR studies for the reported [Re(*p*-NTol)X_2(L)(PPh_3)]. It is likely that electronic effects resulting from differences in ionic radii, polarizabilities and donor

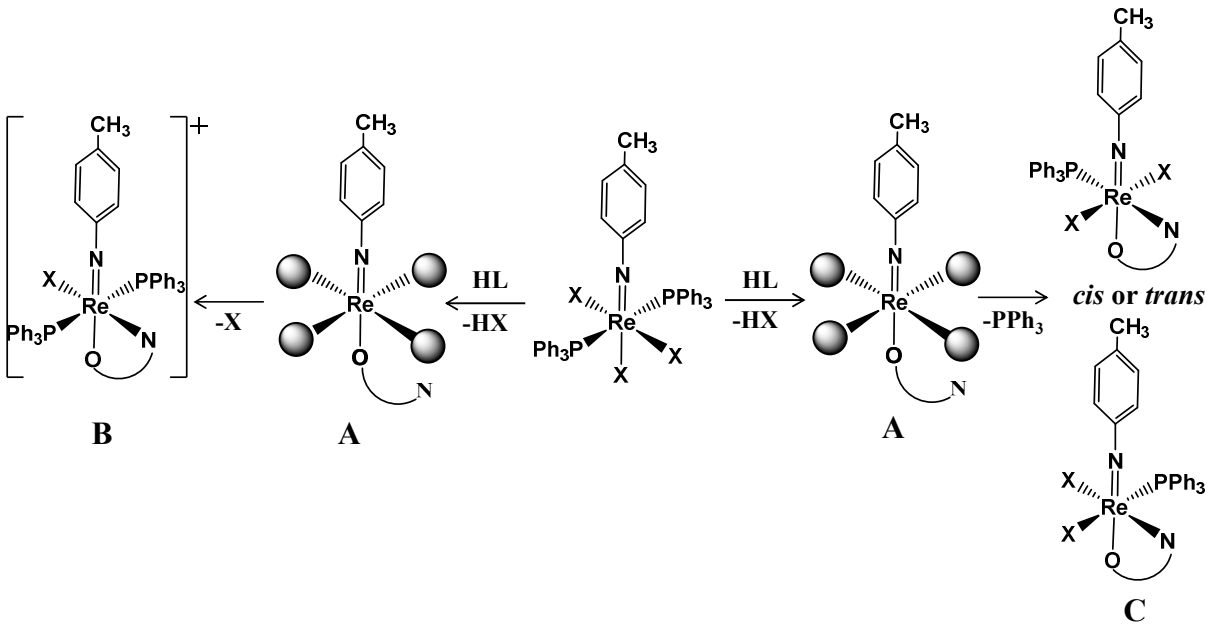
availability of bromide compared to chloride ligands are significant factors responsible for isomeric preferences in the group of complexes [Re(*p*-Ntol)X_2(L)(PPh_3)] incorporating L^1 and L^2 ligands (*cis*-(Cl,Cl)-[Re(*p*-NTol)Cl_2(L)(PPh_3)] and *trans*-(Br,Br)-[Re(*p*-NTol)Br_2(L)(PPh_3)]). In turn, isomeric form (*trans*-*cis*) of [Re(*p*-NTol)X_2(L^3)(PPh_3)] seems to be mainly controlled by electronic factors of the chelating ligand. In this case, both chloride and bromide analogues form *trans*-(X,X)-isomers. The findings concerning [Re(*p*-NTol)X_2(L^3)(PPh_3)] are consistent with those reported for *trans*-(X,X)-[Re(*p*-NTol)X_2(pyz-2-COO)(PPh_3)] and *cis*-(X,X)-[Re(*p*-NTol)X_2(ind-3-COO)(PPh_3)],[18*a*] for which the final structure was independent on halide ions but influenced by the chelating ligand. On contrary, formation of *trans*/*cis*-(X,X) isomers of [Re(*p*-NTol)X_2(py-2-COO)(PPh_3)] was found to be solvent-dependent. Refluxing of [Re(*p*-NTol)X_3(PPh_3)$_2$] with py-2-COOH in methanol led to a mixture of the compounds *trans*-(X,X)-[Re(*p*-NTol)X_2(py-2-COO)(PPh_3)] and *cis*-(X,X)-[Re(*p*-NTol)X_2(py-2-COO)(PPh_3)], whereas the same reactions in methanol resulted in the formation of *trans*-(X,X)-[Re(*p*-NTol)X_2(py-2-COO)(PPh_3)].[18*b*]

Compared with the rhenium(V) imido complexes of carboxylate-based ligands,[18*a–c*] the reactivity of [Re(*p*-NTol)X_3(PPh_3)$_2$] with phenolate-based ligands in methanol was considerably different. In this case, two kinds of products [Re(*p*-NTol)X(L)(PPh_3)$_2$]ReO_4 and [Re(*p*-NTol)X(L)(PPh_3)$_2$]PF_6 were isolated depending on experimental conditions. Addition of NH_4PF_6 salt led to formation of [Re(*p*-NTol)X(L)(PPh_3)$_2$]PF_6, whereas refluxing of [Re(*p*-NTol)X_3(PPh_3)$_2$] with phenolate-based ligands (HL^1, HL^2 and HL^3) in methanol followed by slow solvent evaporation at room temperature resulted in isolation of [Re(*p*-NTol)X(L)(PPh_3)$_2$]ReO_4. The origin of the perrhenate anion in [Re(*p*-NTol)X(L)(PPh_3)$_2$]ReO_4 is probably due to the oxidation of a portion of [Re(*p*-NTol)X(L)(PPh_3)$_2$]X (X = Cl, Br), which is supposed to form in the first step of the reaction. The formation of perrhenate is well documented in the chemistry of rhenium(V) complexes and was confirmed previously for [Re(*p*-NTol)(hmbzim)$_2$(PPh_3)]ReO_4,[19] [$ReOCl_2$(pzH)$_2$($OAsPh_3$)](ReO_4),[20] [ReO(hmbzim)$_2$(PPh_3)](ReO_4),[21] [Re(*p*-NTol)X(OMe)(Hdpa)(PPh_3)]ReO_4.[22]

In both acetonitrile and methanol, the initial step of the complex formation seems to concern the substitution of the oxygen atom of N,O-donor ligand (HL^1, HL^2 and HL^3) for the labile X ligand *trans* to imido group in [Re(*p*-NTol)X_3(PPh_3)$_2$], possibly with the proton transfer to give monodentate intermediate **A** (Scheme 3). In the next step, the uncoordinated N-donor atom of N,O-donor ligand would either substitute the equatorial halide to form a monocationic complexes [Re(*p*-NTol)X(L)(PPh_3)$_2$]X or substitute one of the equatorial phosphine ligands to form neutral imido complexes *trans*-(X,X)-[Re(*p*-NTol)X_2(L)(PPh_3)] or *cis*-(X,X)-[Re(*p*-NTol)X_2(N–O)(PPh_3)]. For reported here uninegative N,O-donor ligands (L^1, L^2 and L^3), both neutral [Re(*p*-NTol)X_2(L)(PPh_3)] and cationic [Re(*p*-NTol)X(L)(PPh_3)$_2$]$^+$

complexes were obtained. On the contrary, the reactions of [Re(*p*-NTol)$X_3(PPh_3)_2$] with chelating carboxylate-based ligands [18a–c] resulted in formation of only neutral [Re(*p*-NTol)X_2(L)(PPh_3)].

Taken together, the studies support that final molecular structure of imido rhenium(V) complexes incorporating uninegative N,O-donor ligands may be tuned by careful selection of L and X ligands as well as experimental conditions. To get a deeper understanding this relationship, however, more research needs to be undertaken.



Scheme 3. Proposed mechanism for the formation of cis or *trans*-(X,X)-[Re(*p*-NTol)X_2(L)(PPh_3)] and [Re(*p*-NTol)X(L)$(PPh_3)_2]^+$.

2.2 Molecular Structures

The crystallographic data of compounds **2**–**10** and **13**–**16** are summarized in Tables 1–3, and the selected bond lengths and angles are gathered in Tables 4–6. The representative molecular structures of [Re(*p*-NTol)X_2(L)(PPh_3)], [Re(*p*-NTol)X(L)$(PPh_3)_2$]ReO_4 and [Re(*p*-NTol)X(L)$(PPh_3)_2$]PF_6 are shown in Fig. 1. The preservative views of molecular structures for remaining compounds were included in the Electronic supplementary information (ESI; Figs. S1–S3).

Table 1 Crystal data and structure refinement for complexes **2–6**

	2	**3**	**4**	**5**	**6**
Empirical formula	$C_{38}H_{32}Br_2N_4OPRe$	$C_{42}H_{36}Cl_2N_4OSPRe$	$C_{38}H_{30}Br_2N_2OPSRe$	$C_{38}H_{30}Cl_2N_2O_2PRe$	$C_{38}H_{30}Br_2N_2O_2PRe$
Formula weight	937.67	932.88	939.69	834.71	923.63
Temperature [K]	293.0(2)	293.0(2)	293.0(2)	298.0(1)	293.0(2)
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	P-1	$P2_1/n$	$P2_1/n$	$P2_1/c$
Unit cell dimensions [Å, °]	a = 10.1990(4)	a = 10.4203(4)	a = 10.0403(4)	a = 9.9154(10)	a = 10.0301(3)
	b = 22.6461(8)	b = 11.1922(4)	b = 22.9911(8)	b = 22.4996(3)	b = 22.6557(7)
	c = 14.8400(6)	c = 17.5181(6)	c = 14.5963(5)	c = 14.6664(2)	c = 17.5430(4)
		α = 80.298(3)			
	β = 90.964(3)	β = 86.888(3)	β = 91.736(3)	β = 92.8070(10)	β = 122.839(2)
		γ = 74.343(3)			
Volume [$Å^3$]	3427.1(2)	1939.04(12)	3367.8(2)	3268.04(7)	3349.42(16)
Z	4	2	4	4	4
Density (calculated) [Mg/m^3]	1.817	1.598	1.853	1.697	1.832
Absorption coefficient [mm^{-1}]	5.962	3.405	6.125	3.969	6.099
F(000)	1824	928	1824	1648	1792
Crystal size [mm]	0.064 x0.069 x 0.094	0.035 x 0.079 x 0.083	0.037 x 0.049 x 0.118	0.060 x 0.120 x 0.380	0.104 x 0.089 x 0.057
θ range for data collection [°]	3.36 to 25.00	3.54 to 25.00	3.31 to 25.00	2.59 to 25.68	3.38 to 25.00
Index ranges	$-12 \le h \le 10$	$-11 \le h \le 12$	$-11 \le h \le 11$	$-12 \le h \le 9$	$-11 \le h \le 11$
	$-26 \le k \le 26$	$-13 \le k \le 13$	$-27 \le k \le 26$	$-27 \le k \le 27$	$-26 \le k \le 23$
	$-17 \le l \le 15$	$-20 \le l \le 20$	$-16 \le l \le 17$	$-17 \le l \le 17$	$-17 \le l \le 16$
Reflections collected	19225	14656	17314	14764	17713
Independent reflections	6030 (R_{int} = 0.0450)	6821 (R_{int} = 0.0621)	5914 (R_{int} = 0.0372)	6152 (R_{int} = 0.0298)	5877 (R_{int} = 0.0377)
Completeness to 2θ=50º [%]	99.8	99.7	99.7		99.7
Max. and min. transmission	0.277 and 1.000	0.789 and 1.000	0.466 and 1.000	0.690 and 1.000	0.403 and 1.000
Data / restraints / parameters	6030 / 0 / 426	6821 / 0 / 472	5914 / 0 / 416	6152 / 0 / 416	5877 / 0 / 416
Goodness-of-fit on F^2	1.065	0.954	1.029	0.920	1.029
Final R indices [I>2σ(I)]	R1 = 0.0321	R1 = 0.0438	R1 = 0.0270	R1 = 0.0199	R1 = 0.0290
	wR2 = 0.0726	wR2 = 0.0837	wR2 = 0.0490		wR2 = 0.0640
R indices (all data)	R1 = 0.0433	R1 = 0.0645	R1 = 0.0398	R1 = 0.0274	R1 = 0.0424
	wR2 = 0.0764	wR2 = 0.0884	wR2 = 0.0518		wR2 = 0.0673
Largest diff. peak and hole[e $Å^{-3}$]	1.236 and -0.773	1.799 and -0.996	0.709 and -0.440	0.875 and -0.749	0.776 and -0.995

Table 2 Crystal data and structure refinement for complexes **7–10**

	7	**8**	**9**	**10**
Empirical formula	$C_{56}H_{47}ClN_4O_5P_2Re_2$	$C_{56}H_{47}BrN_4O_5P_2Re_2$	$C_{56}H_{45}ClN_2O_5P_2SRe_2$	$C_{74}H_{60}BrN_2O_5P_3SRe_2$
Formula weight	1325.77	1370.23	1327.79	1634.52
Temperature [K]	293.0(2)	293.0(2)	293.0(2)	293.0(2)
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	P-1
Unit cell dimensions [Å, °]	a = 12.7856(4)	a = 12.8922(5)	a = 12.7001(3)	a = 11.6599(3)
	b = 20.8513(6)	b = 20.9641(6)	b = 21.0563(4)	b = 17.4480(4)
	c = 20.5169(6)	c = 20.6190(7)	c = 19.9772(5)	c = 18.3654(5)
				α = 99.887(2)
	β = 108.012(3)	β = 106.991(4)	β = 107.282(3)	β = 107.017(2)
				γ = 108.687(2)
Volume [$Å^3$]	5201.7(3)	5329.5(3)	5101.1(2)	3235.74(14)
Z	4	4	4	2
Density (calculated) [Mg/m^3]	1.693	1.730	1.729	1.678
Absorption coefficient [mm^{-1}]	4.815	5.399	4.948	4.515
F(000)	2592	2664	2592	1608
Crystal size [mm]	0.040 x 0.082 x 0.181	0.092 x 0.138 x 0.168	0.028 x 0.082 x 0.177	0.114 x 0.116 x 0.161
θ range for data collection [°]	3.50 to 25.00	3.35 to 25.00	3.29 to 25.00	3.44 to 25.00
Index ranges	$-15 \le h \le 15$	$-14 \le h \le 15$	$-15 \le h \le 15$	$-12 \le h \le 13$
	$-19 \le k \le 24$	$-24 \le k \le 24$	$-24 \le k \le 25$	$-20 \le k \le 20$
	$-24 \le l \le 19$	$-24 \le l \le 22$	$-23 \le l \le 23$	$-21 \le l \le 21$
Reflections collected	28622	26577	27174	28741
Independent reflections	9141 (R_{int} = 0.033)	9371 (R_{int} = 0.0347)	8960 (R_{int} = 0.0323)	11365 (R_{int} = 0.0439)
Completeness to 2θ=50º [%]	99.7	99.7	99.8	99.8
Max. and min. transmission	0.497 and 1.000	0.644 and 1.000	0.454 and 1.000	0.370 and 1.000
Data / restraints / parameters	9141 / 0 / 633	9371 / 0 / 633	8960 / 0 / 623	11365 / 0 / 794
Goodness-of-fit on F^2	1.028	1.042	1.032	1.011
Final R indices [I>2σ(I)]	R1 = 0.0350	R1 = 0.0439	R1 = 0.0375	R1 = 0.0337
	wR2 = 0.0756	wR2 = 0.0992	wR2 = 0.0843	wR2 = 0.0699
R indices (all data)	R1 = 0.0456	R1 = 0.0620	R1 = 0.0507	R1 = 0.0467
	wR2 = 0.0794	wR2 = 0.1052	wR2 = 0.0887	wR2 = 0.0749
Largest diff. peak and hole[e $Å^{-3}$]	2.22 and -2.18	2.608 and -2.749	1.659 and -1.544	1.823 and -1.624

Table 3 Crystal data and structure refinement for complexes **13–16**

	13	**14**	**15**	**16**
Empirical formula	$C_{56}H_{45}ClF_6N_2OP_3ReS$	$C_{56}H_{45}BrF_6N_2OP_3ReS$	$C_{74}H_{60}ClF_6N_2O_2P_4Re$	$C_{74}H_{60}BrF_6N_2O_2P_4Re$
Formula weight	1222.56	1267.02	1468.77	1513.23
Temperature [K]	293.0(2)	293.0(2)	293.0(2)	293.0(2)
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	triclinic	triclinic
Space group	$P2_1/c$	$P2_1/c$	P-1	P-1
Unit cell dimensions [Å, °]	a = 12.2050(4) b = 11.5341(5) c = 36.2386(12) β = 91.344(3)	a = 12.1934(5) b = 11.6623(3) c = 36.0446(12) β = 91.283(4)	a = 11.7939(7) b = 17.2730(7) c = 18.3327(11) α = 99.156(4) β = 107.652(5) γ = 108.436(4)	a = 11.8734(3) b = 17.2825(5) c = 18.3204(5) α = 99.237(2) β = 107.373(2) γ = 108.801(2)
Volume [$Å^3$]	5100.1(3)	5124.4(3)	3239.1(3)	3256.39(15)
Z	4	4	2	2
Density (calculated) [Mg/m^3]	1.592	1.642	1.506	1.543
Absorption coefficient [mm^{-1}]	2.635	3.350	2.082	2.644
F(000)	2440	2512	1480	1516
Crystal size [mm]	0.159 x 0.064 x 0.038	0.388 x 0.078 x 0.052	0.068 x 0.085 x 0.122	0.099 x 0.112 x 0.209
θ range for data collection [°]	3.28 to 25.00	3.49 to 25.00	3.36 to 25.00	3.35 to 25.00
Index ranges	-14<=h<=14 -13<=k<=13 -43<=l<=43	-14 ≤ h ≤14 -13 ≤ k ≤ 12 -42 ≤ l ≤ 36	-14 ≤ h ≤14 -20 ≤ k ≤ 20 -21 ≤ l ≤ 21	-13 ≤ h ≤14 -19 ≤ k ≤ 20 -21 ≤ l ≤ 21
Reflections collected	33240	33339	31414	30772
Independent reflections	8965 (R_{int} = 0.0963)	8996 (R_{int} = 0.0558)	11368 (R_{int} = 0.0889)	11445 (R_{int} = 0.0647)
Completeness to 2θ=50º [%]	99.8	99.7	99.8	99.8
Max. and min. transmission	0.420 and 1.000	0.562 and 1.000	0.817 and 1.000	0.619 and 1.000
Data / restraints / parameters	8965 / 0 / 641	8996 / 0 / 641	11368 / 0 / 812	11445 / 0 / 812
Goodness-of-fit on F^2	1.072	1.168	0.961	1.062
Final R indices [I>2σ(I)]	R1 = 0.0789 wR2 = 0.1525	R1 = 0.0525 wR2 = 0.0850	R1 = 0.0626 wR2 = 0.1306	R1 = 0.0473 wR2 = 0.0991
R indices (all data)	R1 = 0.1062 wR2 = 0.1617	R1 = 0.0657 wR2 = 0.0882	R1 = 0.1013 wR2 = 0.1443	R1 = 0.0661 wR2 = 0.1076
Largest diff. peak and hole[e $Å^{-3}$]	3.571 and -2.327	1.193 and -2.387	2.336 and -0.981	1.796 and -0.798

Table 4 The selected bond lengths [Å] and angles [°] for compounds **2–6**

	2 (X=Br)	**3 (X=Cl)**	**4 (X=Br)**	**5 (X=Cl)**	**6 (X=Br)**
Bond lengths					
Re(1)–N(2)	1.723(4)	1.704(5)	1.725(3)	1.721(2)	1.722(4)
Re(1)–O(1)	1.997(3)	2.008(4)	2.016(3)	2.0113(18)	2.004(3)
Re(1)–N(1)	2.181(4)	2.136(5)	2.186(3)	2.161(2)	2.160(4)
Re(1)–X(1)	2.5445(5)	2.4357(14)	2.5430(4)	2.4190(7)	2.5321(5)
Re(1)–X(2)	2.5610(5)	2.4142(16)	2.5732(4)	2.4014(7)	2.5545(5)
Re(1)–P(1)	2.4279(12)	2.4555(15)	2.4431(10)	2.4339(7)	2.4393(12)
Bond angles					
N(2)–Re(1)–O(1)	177.41(15)	173.54(19)	177.64(12)	177.32(9)	176.88(14)
N(2)–Re(1)–N(1)	96.04(16)	97.2(2)	96.65(13)	96.33(9)	96.12(15)
O(1)–Re(1)–N(1)	81.73(13)	81.78(18)	81.78(11)	81.56(8)	81.47(14)
N(2)–Re(1)–X(1)	94.46(13)	98.94(15)	93.36(10)	96.15(7)	93.63(11)
O(1)–Re(1)–X(1)	84.03(10)	87.35(11)	84.75(7)	85.46(6)	84.20(9)
N(1)–Re(1)–X(1)	84.73(10)	85.14(12)	84.36(8)	88.43(6)	84.43(10)
N(2)–Re(1)–X(2)	96.75(13)	93.15(17)	97.18(10)	94.13(7)	96.46(11)
O(1)–Re(1)–X(2)	84.52(10)	88.62(13)	84.55(7)	84.04(6)	85.45(9)
N(1)–Re(1)–X(2)	87.93(11)	167.71(13)	88.19(8)	84.30(6)	87.82(10)
X(1)–Re(1)–X(2)	167.181(19)	86.77(5)	167.733(15)	168.00(2)	167.878(18)
N(2)–Re(1)–P(1)	92.54(13)	88.83(15)	91.41(10)	91.66(8)	91.83(12)
O(1)–Re(1)–P(1)	89.64(10)	84.97(11)	90.05(8)	90.38(6)	90.49(9)
N(1)–Re(1)–P(1)	171.23(10)	97.00(12)	171.21(9)	171.61(6)	171.53(11)
X(1)–Re(1)–P(1)	92.82(3)	171.64(5)	91.69(3)	93.27(2)	92.17(3)
X(2)–Re(1)–P(1)	92.87(3)	89.75(5)	94.30(3)	92.60(2)	94.22(3)
C(32)–N(2)–Re(1)	174.3(3)	170.5(4)	173.8(3)	172.0(2)	172.4(3)

Table 5 The experimental bond lengths [Å] and angles [°] for compounds **7–10**

	7 (X=Cl)	**8 (X=Br)**	**9 (X=Cl)**	**10 (X=Br)**
Bond lengths				
Re(1)–N(2)	1.731(4)	1.741(5)	1.722(4)	1.732(3)
Re(1)–O(1)	1.972(3)	1.979(4)	1.983(3)	1.974(3)
Re(1)–N(1)	2.136(4)	2.149(5)	2.159(4)	2.147(4)
Re(1)–X(1)	2.3971(14)	2.5516(7)	2.4673(11)	2.5671(5)
Re(1)–P(1)	2.4984(13)	2.5127(17)	2.4956(13)	2.5179(10)
Re(1)–P(2)	2.5075(14)	2.5101(17)	2.5104(13)	2.5268(10)
Re(2)–O(2)	1.668(8)	1.600(11)	1.704(7)	1.696(4)
Re(2)–O(3)	1.653(9)	1.633(11)	1.690(7)	1.690(5)
Re(2)–O(4)	1.696(8)	1.681(7)	1.693(6)	1.642(5)
Re(2)–O(5)	1.683(6)	1.706(10)	1.659(8)	1.699(5)
Bond angles				
N(2)–Re(1)–O(1)	178.48(16)	177.6(2)	176.98(17)	175.76(14)
N(2)–Re(1)–N(1)	98.79(16)	99.5(2)	100.16(17)	100.59(15)
O(1)–Re(1)–N(1)	81.52(14)	81.64(18)	82.79(15)	83.30(13)
N(2)–Re(1)–X(1)	91.05(13)	90.32(16)	89.19(13)	88.78(12)
O(1)–Re(1)–X(1)	88.73(10)	88.72(12)	87.89(11)	87.36(9)
N(1)–Re(1)–X(1)	169.64(11)	169.50(14)	170.46(12)	170.60(9)
N(2)–Re(1)–P(1)	96.25(14)	92.15(17)	96.35(13)	95.25(10)
O(1)–Re(1)–P(1)	85.24(9)	85.68(13)	84.28(10)	86.38(8)
N(1)–Re(1)–P(1)	88.75(11)	91.70(14)	89.96(11)	90.18(8)
X(1)–Re(1)–P(1)	86.96(4)	91.71(4)	87.09(4)	88.19(3)
C(32)–N(2)–Re(1)	171.5(3)	171.6(5)	171.3(4)	168.5(3)
O(1)–Re(1)–P(2)	85.46(9)	85.37(13)	86.90(10)	87.48(8)
N(2)–Re(1)–P(2)	93.04(14)	96.77 (17)	92.33(13)	90.73(10)
N(1)–Re(1)–P(2)	91.96(11)	88.39(14)	91.46(11)	91.32(8)
P(1)–Re(1)–P(2)	170.46(4)	170.94(5)	170.82(4)	173.47(4)
P(2)–Re(1)–X(1)	90.74(4)	86.68(4)	90.05(4)	89.31(3)
O(2)–Re(2)–O(3)	110.9(5)	110.3(7)	109.5(4)	110.1(2)
O(2)–Re(2)–O(4)	108.8(4)	111.6(6)	109.8(3)	111.5(3)
O(2)–Re(2)–O(5)	109.9(4)	107.4(5)	108.7(4)	108.7(3)
O(3)–Re(2)–O(4)	109.9(5)	108.4(6)	107.6(3)	109.4(3)
O(3)–Re(2)–O(5)	108.2(4)	110.5(6)	108.9(5)	107.6(3)
O(4)–Re(2)–O(5)	109.1(4)	108.7(5)	112.3(4)	109.5(4)

Table 6 The selected experimental bond lengths [Å] and angles [°] for **13–16**

	13 (X=Cl)	**14 (X=Br)**	**15 (X=Cl)**	**16 (X=Br)**
Bond lengths				
Re(1)–N(2)	1.734(8)	1.717(5)	1.740(7)	1.731(5)
Re(1)–O(1)	2.002(7)	1.984(4)	1.979(5)	1.974(3)
Re(1)–N(1)	2.161(8)	2.163(5)	2.146(8)	2.141(5)
Re(1)–X(1)	2.409(3)	2.5607(7)	2.407(3)	2.5552(7)
Re(1)–P(1)	2.514(3)	2.5155(17)	2.517(2)	2.5201(16)
Re(1)–P(2)	2.512(3)	2.5160(16)	2.509(2)	2.5097(16)
P(3)–F(1)	1.512(13)	1.540(7)	1.576(11)	1.558(10)
P(3)–F(2)	1.551(11)	1.523(7)	1.501(13)	1.557(8)
P(3)–F(3)	1.525(11)	1.508(7)	1.531(11)	1.559(9)
P(3)–F(4)	1.538(10)	1.562(7)	1.566(11)	1.567(8)
P(3)–F(5)	1.560(11)	1.548(6)	1.533(13)	1.545(10)
P(3)–F(6)	1.531(13)	1.522(6)	1.587(14)	1.557(6)
P(3)–F(1A)			1.561(12)	1.557(9)
P(3)–F(2A)			1.586(10)	1.549(15)
P(3)–F(3A)			1.555(9)	1.553(9)
P(3)–F(4A)			1.553(12)	1.551(11)
P(3)–F(5A)			1.530(10)	1.563(10)
P(3)–F(6A)			1.579(10)	1.569(14)
Bond angles				
N(2)–Re(1)–O(1)	174.9(3)	174.1(2)	177.3(3)	176.97(19)
N(2)–Re(1)–N(1)	101.9(4)	102.9(2)	97.5(3)	98.3(2)
O(1)–Re(1)–N(1)	82.8(3)	82.58(18)	82.6(3)	82.50(17)
N(2)–Re(1)–X(1)	92.1(3)	91.35(16)	91.0(3)	90.40(18)
O(1)–Re(1)–X(1)	83.3(2)	83.25(12)	89.02(19)	88.93(11)
N(1)–Re(1)–X(1)	165.9(3)	165.57(14)	171.5(2)	171.29(14)
N(2)–Re(1)–P(1)	92.2(3)	91.87(16)	92.0(2)	91.25(17)
O(1)–Re(1)–P(1)	89.8(2)	90.16(13)	85.34(15)	85.79(11)
N(1)–Re(1)–P(1)	90.2(2)	89.96(13)	91.85(19)	91.75(10)
X(1)–Re(1)–P(1)	87.27(9)	87.34(4)	88.84(8)	89.11(4)
O(1)–Re(1)–P(2)	90.2(2)	89.79(13)	88.10(15)	87.57(11)
N(2)–Re(1)–P(2)	87.8(3)	88.18(16)	94.6(2)	95.36(17)
N(1)–Re(1)–P(2)	89.8(2)	90.03(13)	89.97(19)	89.85(10)
P(1)–Re(1)–P(2)	179.96(12)	179.95(6)	172.91(8)	172.90(6)
P(2)–Re(1)–X(1)	92.75(9)	92.66(4)	88.36(8)	88.28(4)
C(32)–N(2)–Re(1)	167.9(8)	170.0(4)	169.0(7)	169.4(5)

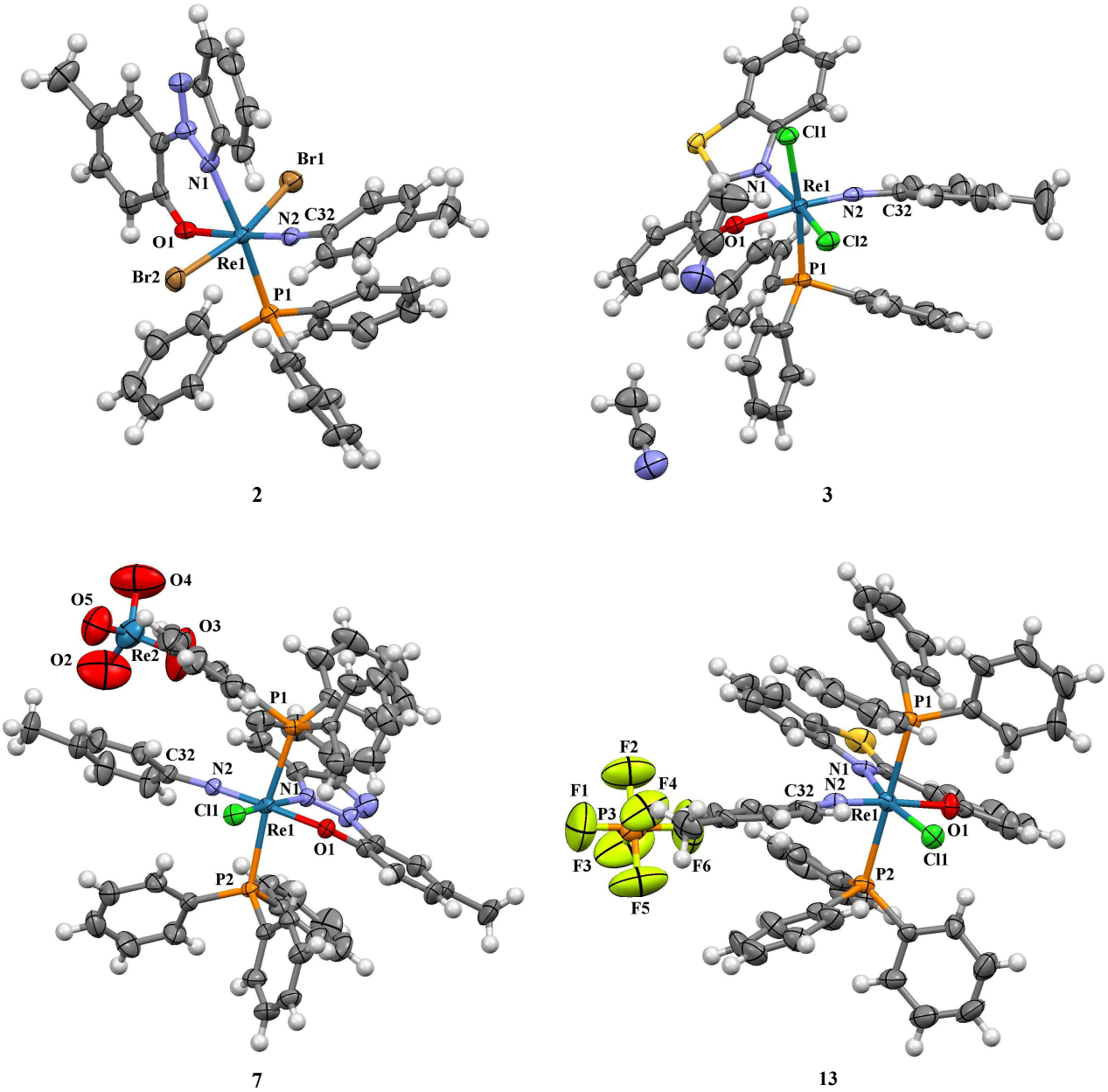


Fig. 1 A perspective view showing the molecular structure of the representative complexes **2**, **3**, **7** and **13**. Displacement ellipsoids are drawn at 50% probability.

Complexes [Re(*p*-NTol)X_2(L)(PPh_3)] (X = Cl, Br; L = L^1, L^2, L^3). The complexes [Re(*p*-NTol)X_2(L)(PPh_3)] (**1**–**6**) show a six coordinate rhenium atom with distorted octahedral geometry defined by the *p*–methylphenylimido group, two halide ions, phosphorus atom of PPh_3 molecule and chelating phenolate-based ligand L^1, L^2 and L^3. The *p*–methylphenylimido (*p*-NTol) ligand is *trans* to the phenolate oxygen atom, which corresponds to a minimum of *trans* weakening caused by the Re=NR multiple bond. Triphenylphosphine molecule with its π-acidity adopts *cis* position with respect to the linear RN=Re–O core and stabilizes it due to accessible π-donation from rhenium to PPh_3 molecule. The repulsion exerted by the Re=NR unit is clearly visible in increasing the angles N(2)–Re–N(1), N(2)–Re–X(1) and N(2)–Re–X(2) beyond 90º. The chelating N–O ligand essentially forms a planar six-membered metallacycle with a bite angle N(1)–Re(1)–O(1) of 80.68(7)° in **1**,[18d] 81.73(13)° in **2**, 81.78(18)° in **3**, 81.78(11)° in **4**, 81.56(8)° in **5** and 81.47(14)° in **6**.

The halide ions of **1** and **3** are in *cis* relative dispositions, whereas the complexes **2**, **4**, **5** and **6** were found to be *trans*-(X,X) isomers. For both *cis*–(X,X) and *trans*–(X,X) isomers of [Re(*p*-NTol)X_2(L)(PPh_3)], the Re–N_{imido}–C_{imido} bond angle of 175.99(18)° in **1**, [18d] 174.3(3)° in **2**, 170.5(4)° in **3**, 174.8(3)° in **4**, 172.0(2)° in **5** and 172.4(3)° in **6** agrees with a linear coordination mode of the arylimido ligands (167–176°), and it is typical of phenyl imido ligands in high oxidation state complexes, in which the metal is relatively electron-deficient and some π-bonding between the imido nitrogen atom and the metal exists.[18, 19, 22, 23]

The Re–N_{imido} bond lengths of 1.7195(20) Å in **1**[18d],1.723(4) Å in **2**, 1.704(5) Å in **3**, 1.725(3) Å in **4**, 1.721(2) Å in **5** and 1.722(4) Å in **6** fall in the range typical of mononuclear complexes of rhenium(V) having $[Re{=}NR]^{3+}$ core.[18, 19, 22, 23] The interatomic distances between the rhenium atom and phenolate oxygen atom of 1.9881(17) Å in **1**[18d], 1.997(3) Å in **2**, 2.008(4) Å in **3**, 2.016(3)Å in **4**, 2.0113(18) Å in **5** and 2.004(3) Å in **6** reflect single bond character,[24] indicating only slight electron delocalization in the RN=Re–O unit. A noticeable difference in Re–O(1) and Re–N(1) of **1**–**6** can be understood in terms of Pearson's hard-soft acid-base theory. The Re(V) (hard Lewis acid) forms stronger bonds with oxygen (hard base) rather than with the comparatively softer base nitrogen. Except for a slight shortening of Re–N(1) in *cis* isomers (**1** and **3**) compared to **2**, **4**, **5** and **6**, no extraordinary differences were noticed in bond lengths between *cis*–(X,X) and *trans*–(X,X) isomers of [Re(*p*-NTol)X_2(L)(PPh_3)].

Complexes [Re(*p*-NTol)X(L)(PPh_3)$_2$]Z (X = Cl, Br; Z = ReO_4^-, PF_6^-). The cation [Re(*p*-NTol)X(L)(PPh_3)$_2$]$^+$ in the compounds **7**–**16** has a distorted octahedral configuration with two *trans*-located triphenylphosphine molecules, chelating uninegative N,O-donor ligand, halide ion and *p*-methylphenylimido ligand. Likewise in the neutral complexes [Re(*p*-NTol)X_2(L)(PPh_3)], the oxygen

atom of the chelating ligand occupies *trans* position to the *p*-methylphenylimido ion and the RN=Re–O core with multiply bonded imido ligand is stabilized due to accessible π-donation from rhenium to triphenylphosphine molecule. The Re(1)–N(2)–C(32) bond angle [171.5(3)° in **7**, 171.6(5)° in **8**, 171.3(4)° in **9**, 168.5(3)° in **10**, 167.9(8)° in **13**, 170.0(4)° in **14**, 169.7(5)° in **15** and 169.3(4)° in **16**] indicates a linear coordination mode of the arylimido ligand in the structures.[19, 20, 23, 24] The Re–N_{imido} bond lengths of **7**–**10** and **13**–**16** [1.731(4) Å in **7**, 1.741(5) Å in **8**, 1.722(4) Å in **9**, 1.732(3) Å in **10**, 1.734(8) Å in **13**, 1.717(5) Å in **14**, 1.740(5) Å in **15** and 1.732(4) Å in **16**] confirm the presence of a triple bond Re–N_{imido}.[18, 19, 22, 23]

Compared to above mentioned [Re(*p*-NTol)X_2(L)(PPh_3)], the interatomic distances between the rhenium atom and the oxygen atom of phenolate-based ligands [1.972(3) Å in **7,** 1.979(4) Å in **8,** 1.983(3) Å in **9**, 1.974(3) Å in **10**, 2.002(7) Å in **13,** 1.984(4) Å in **14,** 1.983(5) Å in **15** and 1.975(3) Å in **16**] are somewhat shorter. A larger delocalization of electron density in the linear RN=Re–O core in **7**–**16** results in less pronounced electron transfer by π donation from rhenium to triphenylphosphine molecule. The Re–P distances of **7**–**10** and **13**–**16** are significantly longer than those found in [Re(*p*-NTol)X_2(L)(PPh_3)] (**1**–**6**), but similar to other rhenium(V) complexes incorporating two *trans* located phosphine ligands. The average value of Re–PPh_3 bond distance calculated for 35 Re(V) complexes with two PPh_3 in *trans* position to each is 2.480(9) Å.[25] The Re–N(1) bond lengths in the [Re(*p*-NTol)X(L)$(PPh_3)_2]^+$ of **7**–**10** and **13**–**16** well correlate with values reported here for *cis*–(X,X)-[Re(*p*-NTol)X_2(L)(PPh_3)].

IR and ^{1}H NMR spectra. Characteristic bands attributed to ν(C=N), ν(C=C) stretching modes of the chelating ligand of **1**–**16** appear in the range 1620–1550 cm^{-1} and they are only slightly shifted with respect to the free ligands.

Intense absorptions associated with the stretching modes of perrhenate ions of [Re(*p*-NTol)X(L)$(PPh_3)_2$]ReO_4 occur at 905 cm^{-1} for **7**, 908 cm^{-1} for **8**, 909 cm^{-1} for **9** and 903 cm^{-1} for **10**. The IR spectra of the complexes [Re(*p*-NTol)X(L)$(PPh_3)_2$]PF_6 exhibit a broad band in the range 830–880 cm^{-1} indicative of PF_6 group. For all compounds **1**–**16**, the *ν*(Re–NTol) stretches are extremely difficult to identify as these vibrations are mixed with $\nu_{C=N}$ and ν_{P-C} modes of PPh_3 and N–O ligands.[18, 19, 22, 23]

The ^{1}H NMR spectra of **1**–**6** confirmed the occurrence of only one isomer in solution. Distinctive signals attributed to the alkyl protons of the *p*-tolylimido group of **2**–**16** and methyl groups attached to the phenolate ring of *hmpbta* ligand in **2**, **7**, **8**, **11** and **12** occur in the ranges 2.37–2.20 ppm and 2.20–2.09 ppm, respectively. The aromatic region of **2**–**16** is dominated by signals of triphenylphosphine protons, which partially obscure protons of the arylimido group and chelating ligand. Comparison of the ^{1}H NMR spectra of [Re(*p*-NTol)X_2(L)(PPh_3)] and [Re(*p*-NTol)X(L)$(PPh_3)_2$]Z compounds shows evidence of a

downfield shift of the signals of the phenolate-based ligands in the former one. This behaviour indicates stronger interactions between rhenium and chelating ligand in [Re(*p*-NTol)X(L)$(PPh_3)_2$]Z compounds. The lack of paramagnetic broadening or shifts of resonances in the ^{1}H NMR spectra confirms diamagnetism of the complexes **2**–1**6**.

The coordination of the phosphine in **2**–1**6** was additionally confirmed by ^{31}P NMR spectroscopy. The single peaks attributed to the coordinated phosphine were observed in the complexes [Re(*p*-NTol)X_2(L)(PPh_3)] and [Re(*p*-NTol)X(L)$(PPh_3)_2$]Z in the range 25.53–26.27 ppm and 25.57–25.65 ppm. As expected, these phosphorous signals are downfield from uncoordinated triphenylphosphine (–6 ppm) and upfield from triphenylphosphine oxide (29.8 ppm).

2.3 Oxidation of alcohols with *tert*-BuOOH catalyzed by certain rhenium complexes

Complexes of various transition metals are well-known catalysts for oxidations of alcohols [26] and hydrocarbons [27,28] with peroxides. We explored the catalytic activity of complexes **11**–**16** in the oxidation of alcohols and alkanes by aqueous hydrogen peroxide and *tert*-BuOOH (TBHP) under mild conditions. All these rhenium complexes turned out to be almost inactive in oxidation with H_2O_2 (50% aqueous) in acetonitrile at 50–70 ºC. We were unable to oxidize benzene under the same conditions using either hydrogen peroxide or TBHP. In contrast, certain complexes exhibited high activity in oxidation of alcohols with TBHP. It is noteworthy that only two compounds, **13** and **14**, are efficient catalysts in the oxidation of 1-phenylethanol to acetophenone:

$$PhCH(OH)CH_3 + \textit{tert}\text{-BuOOH} + O_2 \rightarrow PhC(=O)CH_3$$

Activity of complexes **15** and **16** is lower, whereas in the presence of compounds **11** and **12** the rate of 1-phenylethanol oxidation is equal to that in the absence of any catalyst. Concentrations of acetophenone after 1 h and the initial reaction rates $W_0 = d[PhC(=O)CH_3]/dt$ are summarized in Table 7.

Table 7 Comparison of complexes **11–16** as catalyst in the oxidation of 1-phenylethanol to acetophenone [a]

Entry	Catalyst	Concentration of $PhC(=O)CH_3$, M	Rate $10^5 \times d[PhC(=O)CH_3]/dt$, M s^{-1}
1	**13**	0.06	1.7
2	**14**	0.014	0.38
3	**15**	0.009	0.25
4	**16**	0.008	0.22
5	**11**	0.007	0.20
6	**12**	0.003	0.008
7	None	0.003	0.008

[a] Conditions. Catalyst concentration, 1×10^{-3} M; 1-phenylethanol, 0.36 M; TBHP (70% aqueous) 1.67 M; 1 h at 70 ºC.

Oxidation properties of complex **13** were studied in more detail. The oxidation of 1-phenylethanol to produce acetophenone with TBHP catalyzed by compound **13** is presented in Fig. 2. Yield of acetophenone is 80% based on the initial 1-phenylethanol, TON attained 290 after 30 h and initial TOF was 60 h^{-1}.

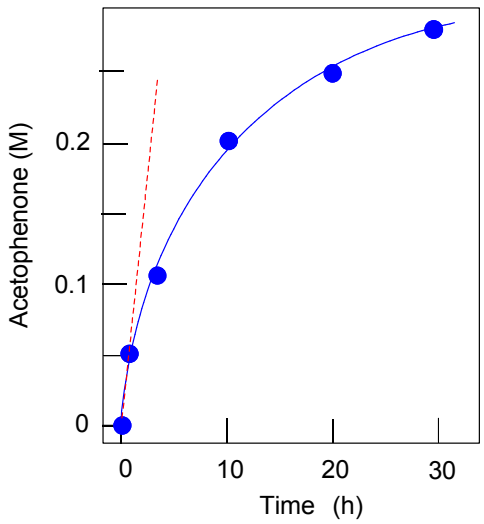


Fig. 2 Accumulation of acetophenone in the oxidation of 1-phenylethanol (0.36 M) with TBHP (1.67 M) catalyzed by compound **13** (1×10^{-3} M) in acetonitrile solution at 70 °C. The initial rate W_0 was determined from the slope of the tangent (in an example shown as dotted straight line) to the kinetic curve of acetophenone accumulation.

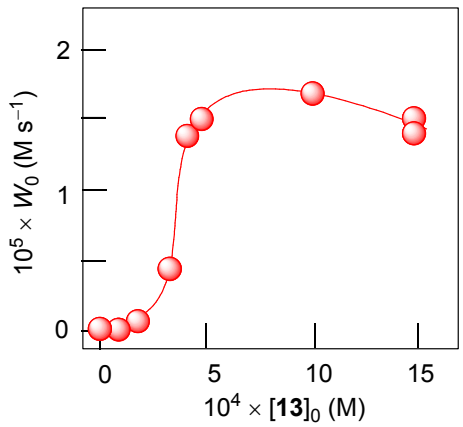


Fig. 3 Dependence of the initial oxidation rate W_0 on initial concentration of compound **13** in the oxidation of 1-phenylethanol (initial concentration 0.36 M) with TBHP (initial concentration 1.67 M) at 70 °C in acetonitrile solution catalyzed by compound **13**.

The dependence of initial reaction rate W_0 on the initial concentration of catalyst **13** is shown in Fig. 3. It can be seen that this dependence is of a sigmoid-type that is at $[\mathbf{13}]_0 \leq 5 \times 10^{-4}$ M the order of the reaction rate relative to **13** is higher than first order.

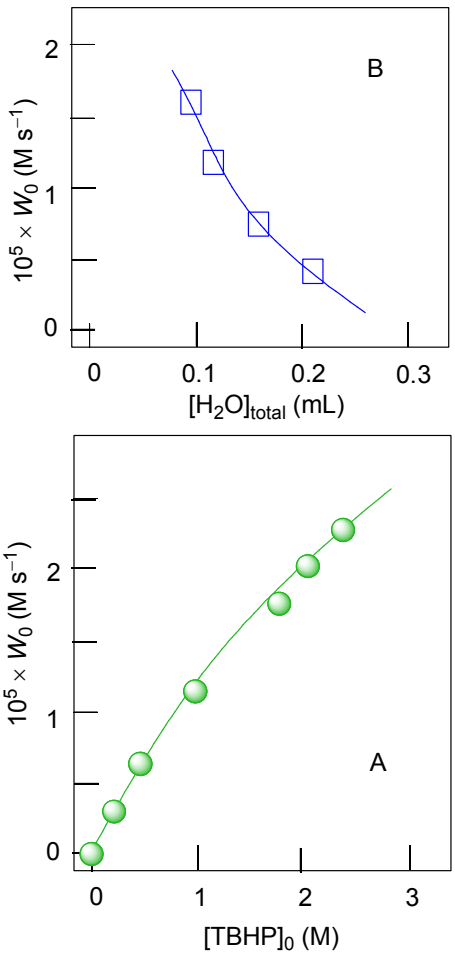


Fig. 4 Graph A: dependence of the initial oxidation rate W_0 on initial concentration of TBHP in the oxidation of 1-phenylethanol (initial concentration 0.25 M) with TBHP (at fixed water concentration) catalyzed by compound **13** (1 × 10^{-3} M) at 70 °C in acetonitrile solution. Graph B: effect of water on the initial rate.

Dependences of initial rates on initial concentrtions of TBHP and 1-phenylethanol are presented in Figs. 4 and 5, respectively. Experiments with different concentrations of TBHP were carried out at fixed total concentration of water. The mode of dependence of W_0 on the initial concentration of TBHP indicates [29] the formation of an intermediate adduct between the catalyst **13** and TBHP followed by subsequent decomposition of the adduct to generate an intermediate species *tert*-BuO$^{\bullet}$ which induces the alcohol oxidation:

TBHP + **13** $\rightleftharpoons$ *Adduct* (equilibrium constant K_1) (1)

Adduct → → *tert*-BuO$^{\bullet}$ (rate constant k_2) (2)

The dependence mode of the initial oxidation rate on 1-phenylethanol concentration reflects [29] a competition between the alcohol and solvent acetonitrile for the interaction with the oxidizing species *tert*-BuO$^{\bullet}$ generated in reaction (2):

tert-BuO$^{\bullet}$ + 1-phenylethanol → products (3)

tert-BuO$^{\bullet}$ + CH_3CN → products (4)

In quasi-stationary approach relative concentration of *tert*-BuO$^{\bullet}$ we can obtain expression (5) for the initial oxidation rate:

$$\frac{d[PhCH(OH)CH_3]}{dt} = W_0 = \frac{W_2}{1 + \dfrac{k_4[CH_3CN]}{k_5[PhCH(OH)CH_3]_0}} \qquad (5)$$

where W_2 is the rate of reaction (2).

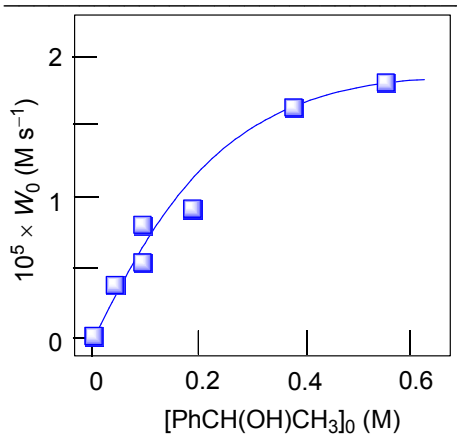


Fig. 5 Dependence of the initial oxidation rate W_0 on initial concentration of 1-phenylethanol in the oxidation of 1-phenylethanol with TBHP (initial concentration 1.67 M) catalyzed by compound **13** (1 × 10^{-3} M) at 70 °C in acetonitrile solution.

Aliphatic alcohols, both cyclic (cyclooctanol) and linear (2-octanol) ones, can be also transformed into the corresponding ketones in the reaction with the TBHP/**13** system. Some examples are presented in Figs. 6 and 7. The yield of cyclooctanone attained 88% after 14 h (Fig. 6, curve 3). In the presence of

nitric acid the oxidation is slower (compare Fig. 6, curves 1 and 2). Linear 2-octanol is transformed into 2-octanone. Compounds **11, 12** and **14** are less efficient catalysts (Fig. 8).

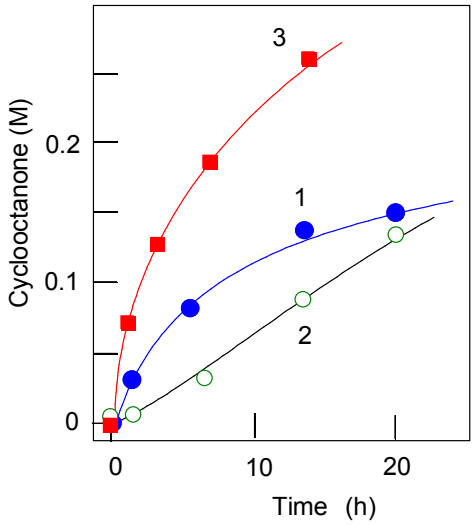


Fig. 6 Accumulation of cyclooctanone in the oxidation of cyclooctanol with TBHP (1.67 M) catalyzed by compound **13** in acetonitrile solution. Conditions. [**13**]$_0$ = 2 × 10^{-3} M, [cyclooctanol]$_0$ = 0.6 M, 60 °C (curve 1); 1 × 10^{-3} M, [cyclooctanol]$_0$ = 0.6 M, [HNO_3]$_{added}$ = 0.05 M, 60 °C (curve 2); [**13**]$_0$ = 1 × 10^{-3} M, [cyclooctanol]$_0$ = 0.3 M, 70 °C (curve 3). Yield of cyclooctanone is 88% after 14 h.

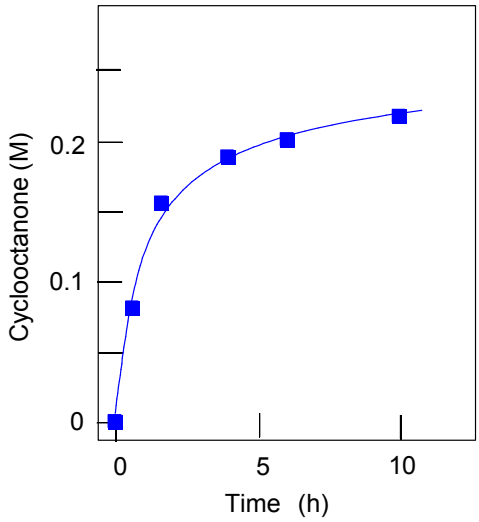


Fig. 7 Accumulation of 2-octanone in the oxidation of 2-octanol (0.6 M) with TBHP (1.67 M) catalyzed by compound **13** (1 × 10^{-3} M) in acetonitrile solution. at 60 °C .

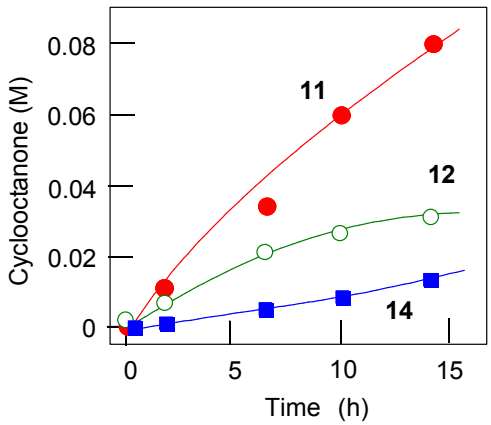


Fig. 8 Accumulation of cyclooctanone in the oxidation of cyclooctanol (0.3 M) with TBHP (1.67 M) in acetonitrile solution catalyzed by compounds (1×10^{-3} M) **11** (60 °C), **12** (70 °C) and **14** (60 °C).

2.4 Catalytic oxidation of alkanes with *tert*-BuOOH

Many works have been devoted to the oxygenation of alkanes with peroxides, particularly, with TBHP.[30,31] The oxygenation of saturated hydrocarbons as well as of some alkane derivatives usually gives rise to the formation of the corresponding alkyl hydroperoxide, ROOH, as the main primary product. To demonstrate the formation of alkyl hydroperoxide in this oxidation and to estimate its concentration in the course of the reaction we used a simple method developed earlier by one of us.[32] If an excess of solid PPh_3 is added to the sample of the reaction solution before the GC analysis, the alkyl hydroperoxide present is completely reduced to the corresponding alcohol. Comparing measured by the GC concentrations of the alcohol and ketone before and after reduction with PPh_3 we can estimate the real concentrations of the three products (alkyl hydroperoxide, ketone and alcohol) present in the reaction solution. In many experiments we determined concentrations of isomers only after reduction with PPh_3.

Complexes **11**–**16** turned out to be less efficient in oxidation of alkanes in comparison with their activity as catalysts for the alcohol oxidation. Turnover numbers attained only 20–30 after 2–4 h. In order to determine the nature of the alkane oxidizing species we measured the selectivity parameters in oxidations of certain alkanes with TBHP catalyzed by compounds **11**–**16**. These values for the oxidation of linear heptane and octane (Table 8, entries 1–8) can be compared with the parameters determined previously [33] for other systems which are also given in Table 8 for comparison. These parameters are slightly higher in comparison with the selectivities determined previously for the systems generating free hydroxyl radicals (entries 9–24) and they are comparable with parameters obtained for other metal-catalyzed oxidations with TBHP (entries 25 and 26). Enhanced selectivities in experiments reflected by entries 27 and 28 (as well as 20) can be due to sterical hindrance. Careful examination selectivity

parameters for the oxidation with TBHP catalyzed rhenium complexes prepared in this work, especially, reflected in entries 4 and 5 show enhanced reactivity C–H bonds in position 2. Similar situation, although more strongly pronounced, was found in the profiles for oxidation with catalysts containing sterically hindered reaction centers (compare profiles presented in Fig. S5).

Table 8 Regioselectivity parameters for oxidation of *n*-heptane or *n*-octane with TBHP or H_2O_2 catalyzed by complexes prepared in this work and (for comparison) by certain other systems [a]

Entry	System	Alkane	TON	C(1):C(2):C(3):C(4)	Ref.
1	**11**-TBHP	Heptane	20	1 : 7.5 : 5.0 : 3.3	This work
2	**12**-TBHP	Heptane	20	1 : 8.3 : 6.3 : 6.0	This work
3	**13**-TBHP	Heptane	22	1 : 13.2 : 8.8 : 5.9	This work
4	**13**-TBHP	Octane (no HNO_3)	16	1 : 6.8 : 3.6 : 2.8	This work
5	**13**-TBHP	Octane (with HNO_3)	23	1 : 3.8 : 1.9 : 1.5	This work
6	**14**-TBHP	Heptane	20	1 : 8.2 : 5.4 : 5.0	This work
7	**15**-TBHP	Heptane	19	1 : 8.5 : 6.5 : 5.0	This work
8	**16**-TBHP	Heptane	13	1 : 9.1 : 5.3 : 4.4	This work
9	hν/H_2O_2	Heptane		1 : 7.0 :6.0 : 7.0	33*a*
10	(*n*-Bu_4N)VO_3/PCA/H_2O_2	Heptane		1 : 9.0 : 7.0 : 7.0	33*a-c*
11	[(η^6-*p*-cym)$OsCl_2$]$_2$/py/H_2O_2	Octane		1 : 2.8 : 2.8 : 2.6	33*d*
12	(η^6-*p*-cym)Os(py)Cl_2/py/H_2O_2	Octane		1.0 : 4.7 : 4.8 : 4.3	33e
13	$Os_3(CO)_{12}$/py/H_2O_2	Octane		1 : 4.0 : 4.0 : 4.0	10*f*,33*f*
14	"**Os**"/H_2O_2	Heptane		1 : 5.5 : 5.0 : 4.5	33g
15	Cp*$_2$Os/py/H_2O_2	Heptane		1 : 7.0 : 7.0 : 7.0	33h
16	$FeSO_4$/H_2O_2	Heptane		1 : 5.0 : 5.0 :4.5	33a,i
17	Fe_2(HPTB)/PCA/H_2O_2	Heptane		1 : 6.0 : 6.0 : 5.0	33j
18	"**Fe-S-Fe**"/PCA/py/H_2O_2	Heptane		1:6.5:6.5:6	33k
19	"**Fe_2**"/H_2O_2	Heptane		1 : 10.0 : 10.0 : 6.0	33l
20	"**Fe_4**"/H_2O_2	Heptane		1 : 15.0 : 14.0 : 11.0	33l
21	"**Re-ind**"/H_2O_2	Octane		1 : 6.0 : 6.0 : 5.0	18*a*
22	$Al(NO_3)_3$/H_2O_2	Heptane		1 : 5.3 : 5.4 : 4.9	33m
23	$Al(NO_3)_3$/H_2O_2	Octane		1 : 5.6 : 5.6 : 5.0	33m
24	$Bi(NO_3)_3$/HNO_3/H_2O_2	Octane		1.0 : 4.4 : 4.3 : 4.0	33n
25	Cu(H_3L^3)(NCS)/TBHP	Octane		1 : 12.0 : 8.0 : 7.0	33o
25	**"Cu_4-O-Si"**/TBHP	Octane		1 :10.5 : 8.2 :7.0	33p
27	"**Cu_4-N**"/TBHP	Heptane		1 : 34 : 23 : 21	33q
28	"**Cu_4-N**"/TBHP	Octane		1 : 65 : 32 : 30	33q

[a] Parameters C(1):C(2):C(3):C(4) are relative normalized reactivities of H atoms at carbon atoms C(1), C(2), C(3) and C(4) of *n*-heptane or *n*-octane chain. All parameters were measured after reduction of the reaction mixtures with PPh_3 before GC analysis and calculated based on the ratios of isomeric alcohols.
[b] Abbreviations. Symbol hν means UV irradiation. PCA is pyrazine-2-carboxylic acid. π-*p*-cym is *p*-cymene. Cp^*_2Os is decamethylosmocene. "**Os**" is complex (2,3-η-1,4-diphenylbut-2-en-1,4-dione)undecacarbonyl triangulotriosmium. Fe_2(HPTB) is complex $[Fe_2(HPTB)(\mu\text{-}OH)(NO_3)_2](NO_3)_2$, HPTB = N,N,N',N'-tetrakis(2-benzimidazolylmethyl)-2-hydroxo-1,3-diaminopropane. "**Fe-S-Fe**" is $(OC)_3Fe(\mu\text{-}PhS)_2Fe(CO)_3$. "**$Fe_2$**" is binuclear complex $[Fe_2(N_3O\text{-}L^1)_2(\mu\text{-}O)(\mu\text{-}OOCCH_3)]^+$, where L^1 = 1-carboxymethyl-4,7-dimethyl-1,4,7-triazacyclononane. "**Fe_4**" is tetranuclear complex $[Fe_4(N_3O_2\text{-}L)_4(\mu\text{-}O)_2]^{4+}$ with ligand $N_3O_2\text{-}L^1$. Complex "**Re-ind**" is *cis*-(Cl,Cl)-$[Re(p\text{-}NC_6H_4CH_3)Cl_2(ind\text{-}3\text{-}COO)(PPh_3)]\cdot 2MeOH$ (where ind-3-COOH is indazole-3-carboxylic acid). In the complex $Cu(H_3L^3)(NCS)$, ligand H_4L^3 is N,N,N′,N′-tetrakis-(2-hydroxyethyl)ethylenediamine. **"Cu_4-O-Si"** is $[(PhSiO_{1.5})_{12}(CuO)_4(NaO_{0.5})_4]$. "**$Cu_4$-N**" is tetracopper(II) triethanolaminate complex $[O\subset Cu_4\{N(CH_2CH_2O)_3\}_4(BOH)_4][BF_4]_2$.

The oxidation with TBHP catalyzed by the rhenium complexes of *cis*-1,2-DMCH and *trans*-1,2-DMCH (where DMCH is dimethylcyclohexane) proceeds non-stereoselectively. Thus, parameter *trans*/*cis* for the oxidation of *cis*-1,2-DMCH catalyzed by **12** was 0.8 and for *trans*-1,2-DMCH it was 0.75. For the catalysis by **13** in the case of *cis*-1,2-DMCH *trans*/*cis* was 0.7. Thus, we can conclude that selectivity parameters testify that in the main pathway alkanes are oxidized by the systems under discussion with the participation of *tert*-butoxyl radicals.

The oxygenation of methylcyclohexane (MCH) proceeds mainly at the tertiary carbon atom with formation of 1-methylcyclohexanol after reduction with PPh_3 (product **P5**; see the ESI, Figs. S5a and S5b). It should be noted that in the oxidation with TBHP catalyzed by complex **13** (Fig. S5bA) as well as oxidation with H_2O_2 catalyzed by complex *cis*-(Cl,Cl)-$[Re(p\text{-}NC_6H_4CH_3)Cl_2(ind\text{-}3\text{-}COO)(PPh_3)]\cdot 2MeOH$ (Fig. S5bB) the position 2 (products **P6** and **P7**) relative to the methyl group of the substrate is less reactive than the corresponding positions 3 (**P8** and **P10**) and 4 (**P9** and **P11**) comparing the formation of isomeric alcohols. This can be explained by some sterical hindrance which is apparently due to the involvement of a bulky oxidizing species. Indeed, products **P6** and **P7** are formed in relatively high concentration in the oxidations with H_2O_2 catalyzed by the osmium complexes (Fig. S5bK,L) and bismuth salt (Fig. S5bJ). At the same time concentration of isomers **P6** and **P7** in the reactions with TBHP catalyzed by bulky catalysts (Fig. S5bD,E,G) are low.

3. Conclusions

The reactivity of [Re(*p*-NTol)$X_3(PPh_3)_2$] (X = Cl, Br) towards phenolate-based chelating ligands (2-(2-hydroxy-5-methylphenyl)benzotriazole, 2-(2-hydroxyphenyl)benzothiazole, and 2-(2-hydroxyphenyl)benzoxazole) has been examined and compared with the related exchange reactions performed with carboxylate-based N,O-donor ligands. As a result of these studies, 15 novel rhenium(V) imidocomplexes have been obtained and characterized structurally and spectroscopically. The findings enhance our understanding of the structural preferences of the imido rhenium(V) complexes with uninegative N,O-donor ligands. Different tested complexes exhibited different catalytic activities in oxidation of alcohols and alkanes with TBHP in acetonitrile. Experiments with methylcyclohexane led to a conclusion that some sterical hindrance exhists around the reaction center.

4. Experimental

4.1 Materials

All chemicals and bidentate ligands were purchased from commercial sources and were used without further purification. The complexes *mer*-[Re(*p*-NTol)$X_3(PPh_3)_2$] (X =Cl, Br) were prepared according to the literature methods.[34]

4.2 Instrumentation

IR spectra were recorded on a Nicolet iS5 spectrophotometer in the spectral range 4000-400cm^{-1} with the samples in form of KBr pellets. The ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra were recorded (298 K) on Bruker Avance 500 NMR spectrometer at a resonance frequency of 500 MHz for ^{1}H NMR spectra, 125 MHz for ^{13}C NMR spectra and 162 MHz for ^{31}P NMR using DMSO-d_6 or $CDCl_3$ as solvent and TMS as an internal solvent. The X-ray intensity data of **2-16** were collected on a Gemini A Ultra diffractometer equipped with Atlas CCD detector and graphite monochromated MoK_α radiation (λ = 0.71073Å) at room temperature. Details concerning crystal data and refinement are given in Table 1. Lorentz, polarization and empirical absorption correction using spherical harmonics implemented in SCALE3 ABSPACK scaling algorithm were applied.[35] The structures were solved by the Patterson method and refined by full-matrix least-squares on F^2 using SHELXL97.[36] All the non-hydrogen atoms were refined anisotropically using full-matrix, least-squares technique. The hydrogen atoms were treated as „riding" on their parent carbon atoms and assigned isotropic temperature factors equal 1.2 (non-methyl) and 1.5 (methyl) times the value of equivalent temperature factor of the parent atom. The methyl groups were allowed to rotate about their local threefold axis. Largest residual electron density in the examined structures is located close to the heavy atoms. In the compounds **15** and **16**, the carbon atoms of one phenyl ring of the

triphenylphosphine molecule and the fluorine anions of hexafluorophosphate show symptoms of disorder, exhibiting in the revolution (prolation and oblation) of the anisotropic displacement ellipsoids.

CCDC- 1422185 (for **2**), - 1422179 (for **3**), - 1422180 (for **4**), - 1422176 (for **5**), - 1422182 (for **6**), - 1422178 (for **7**), - 1422177 (for **8**), - 1422183 (for **9**), - 1422181 (for **10**), - 1422188 (for **13**), - 1422187 (for **14**), - 1422186 (for **15**) and - 1422184 (for **16**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

4.3 Preparation of complexes 2-6

mer-[Re(*p*-NTol)$X_3(PPh_3)_2$] (0.54 mmol) was added to the corresponding phenolate-based ligand (0.60 mmol) in acetonitrile (60 mL) and the reaction mixture was refluxed for 4 h. The resulting solution was reduced in volume to 10 mL and allowed to cool to room temperature. A crystalline precipitate of compound **2**–**6** was filtered off and dried in the air. X-ray quality brown crystals of **2**–**6** were obtained by slow recrystallization from acetonitrile.

***trans*-(Br,Br)-[Re(*p*-NTol)$Br_2(L^1)(PPh_3)$] (2).** (0.52 g of [Re(*p*-NTol)$Br_3(PPh_3)_2$] and 0.13 g of 2-(2-hydroxy-5-methylphenyl)benzotriazole yielded to 370 mg of **2**; yield 80%). $C_{38}H_{32}Br_2N_4OPRe$ (937.67 g/mol): calcd. C 48.67, H 3.44, N 5.97 %; found C 48.37, H 3.32, N 5.69 %. IR (KBr; ν/cm^{-1}): 3055(w), 1610(w), 1587(w), 1503(s), 1496(s), 1481(sh), 1432(m), 1349(w), 1336(w), 1311(m), 1295(w), 1274(w), 1260(m), 1207(w), 1187(w), 1171(w), 1132(w), 1090(w), 1074(sh), 1028(w), 1012(w), 997(w), 904(w), 836(sh), 824(s), 784(w), 744(s), 705(sh), 691(s), 638(w), 616(m), 557(w), 528(vs), 499(m) and 458(w).
^{1}H NMR (DMSO, ppm): δ = 8.04(d, 1H, 8.8Hz), 7.62(dd, 4H, 11.5, 7.2Hz), 7.59 – 7.50(m, 3H), 7.47(t, 2H), 7.39(s, 4H), 7.29(dd, 11H, 19.9, 8.5Hz), 7.08 – 6.99(m, 1H), 2.32(s, 3H) and 2.20(s, 3H).
^{13}C NMR (125 MHz, DMSO-d_6): δ = 148.5, 143.7, 141.8, 133.8, 133.7, 133.6, 133.2, 132.5, 132.4, 131.9, 131.8, 129.5, 129.2, 129.0, 127.9, 124.5, 120.1, 118.2, 117.4, 20.7, 20.4 ppm.
^{31}P NMR (DMSO-d_6): δ = 26.08 ppm.

***cis*-(Cl,Cl)-[Re(*p*-NTol)$Cl_2(L^2)(PPh_3)$]·2MeCN (3)**. (0.43 g of [Re(*p*-NTol)$Cl_3(PPh_3)_2$] and 0.14 g of 2-(2-hydroxyphenyl)benzothiazole yielded to 347 mg of **3**; yield 80%). $C_{42}H_{36}Cl_2N_4OSPRe$ (932.88 g/mol): calcd. C 54.07, H 3.89, N 6.01%; found C 54.42, H 3.78, N 5.89 %. IR (KBr; ν/cm^{-1}): 3060(w), 1592(w), 1572(w), 1481(m), 1472(sh), 1454(sh), 1434(s), 1328(w), 1287(w), 1268(w), 1253(sh),

1231(w), 1192(w), 1170(w), 1127(sh), 1089(m), 1073(sh), 1029(w), 1016(w), 998(w), 842(w), 822(m), 745(s), 703(sh), 694(vs), 650(sh), 618(w), 573(w), 561(w), 520(vs), 508(s), 494(m), 458(w) and 445(w).
^{1}H NMR (DMSO, ppm): δ = 8.61(d, 1H, 9.0Hz), 8.25 – 8.18(m, 1H), 7.92(d, 1H, 7.7Hz), 7.73 – 7.65(m, 5H), 7.53(dd, 10H, 14.4, 6.0Hz), 7.43(d, 3H, 8.3Hz), 7.24(t, 1H, 7.7Hz), 7.04(d, 3H, 8.3Hz), 6.95(t, 1H, 7.3Hz), 5.89(d, 1H, 8.0Hz), 2.68(s, 3H), 2.33(s, 3H) and 2.16(s, 3H).
^{13}C NMR (125 MHz, DMSO-d_6): δ = 153.0, 151.5, 138.2, 134.0, 133.9, 133.3, 132.5, 131.9, 130.9, 130.5, 129.7, 129.2, 129.0, 128.7, 128.6, 127.6, 124.7, 123.5, 122.8, 121.4, 119.2, 118.5, 21.9 ppm.
^{31}P NMR (DMSO-d_6): δ = 25.90 ppm.

***trans*-(Br,Br)-[Re(*p*-NTol)Br$_2$(L^2)(PPh$_3$)] (4)**. (0.52 g of [Re(*p*-NTol)$Br_3(PPh_3)_2$] and 0.14 g of 2-(2-hydroxyphenyl)benzothiazole yielded to 347 mg of **4**; yield 75%). $C_{38}H_{30}Br_2N_2OPSRe$ (939.69 g/mol): calcd. C 48.57, H 3.22, N 2.98 %; found C 48.71, H 3.29, N 2.83 %.
IR (KBr; ν/cm^{-1}): 3059(w), 1593(w), 1553(w), 1479(sh), 1471(s), 1453(sh), 1444(sh), 1433(m), 1413(w), 1350(w), 1327(w), 1290(w), 1276(w), 1220(w), 1187(w), 1172(w), 1150(w), 1126(w), 1101(sh), 1089(w), 1072(sh), 1027(w), 1014(w), 997(w), 984(sh), 955(w), 891(w), 845(w), 824(w), 759(sh), 747(s), 729(sh), 717(sh), 693(s), 622(m), 572(w), 563(sh), 528(vs), 499(m) and 459(w).
^{1}H NMR ($CDCl_3$, ppm): δ = 8.68(d, 1H, 8.3Hz), 7.97 – 7.76(m, 8H), 7.48 – 7.31(m, 13H), 7.19(t, 1H, 7.6Hz), 6.90(d, 3H, 7.8Hz), 6.05(d, 1H, 8.1Hz) and 2.21(s, 3H).
^{31}P NMR ($CDCl_3$): δ = 26.27 ppm.
^{13}C NMR spectrum of **4** was not recorded due to its low solubility in deuterated solvents.

***trans*-(Cl,Cl)-[Re(*p*-NTol)Cl$_2$(L^3)(PPh$_3$)] (5)**. (0.43 g of [Re(*p*-NTol)$Cl_3(PPh_3)_2$] and 0.13 g of 2-(2-hydroxyphenyl)benzoxazole yielded to 347 mg of **5**; yield 80%). $C_{38}H_{30}Cl_2N_2O_2PRe$ (834.71 g/mol): calcd. C 54.68, H 3.62, N 3.36 %; found C 54.83, H 3.57, N 3.49 %.
IR (KBr; ν/cm^{-1}): 3058(w), 1607(m), 1592(m), 1560(w), 1534(m), 1473(vs), 1458(sh), 1432(s), 1352(w), 1334(w), 1315(s), 1261(s), 1249(sh), 1187(w), 1171(w), 1153(w), 1130(w), 1101(sh), 1092(m), 1068(w), 1030(w), 1015(w), 997(w), 873(m), 855(sh), 824(w), 809(w), 758(sh), 751(sh), 742(vs), 692(s), 669(sh), 620(m), 560(w), 529(vs), 500(m), 486(sh), 474(sh), 458(sh), 441(w), 426(w).
^{1}H NMR ($CDCl_3$, ppm): δ = 8.08(d, 1H, 8.0Hz), 7.90-7.81(m, 6H), 7.78(d, 1H, 8.2Hz,), 7.63(d, 1H, 8.0Hz), 7.48-7.34(m, 12H), 7.22(dd, 2H, 14.5; 7.2Hz), 6.96(d, 3H, 8.0Hz), 6.20(d, 1H, 8.4Hz), 2.26(s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ = 164.7, 155.5, 149.3, 135.4, 135.0, 134.9, 130.6, 129.9, 128.0, 127.9, 125.7, 125.6, 122.9, 119.4, 111.2, 22.1 ppm.
^{31}P NMR ($CDCl_3$): δ = 26.07 ppm.

***trans*-(Br,Br)-[Re(*p*-NTol)Br$_2$(L^3)(PPh$_3$)] (6)**. (0.52 g of [Re(*p*-NTol)Br$_3$(PPh$_3$)$_2$] and 0.13 g of 2-(2-hydroxyphenyl)benzoxazole yielded to 370 mg of **6**; yield 80%). $C_{38}H_{30}Br_2N_2O_2PRe$ (923.63 g/mol): calcd. C 49.41, H 3.27, N 3.03%; found C 49.32, H 3.39, N 3.19 %.

IR (KBr; ν/cm^{-1}): 3057(w), 1607(m), 1592(m), 1561(w), 1534(m), 1473(vs), 1458(sh), 1432(s), 1352(w), 1314(s), 1259(s), 1249(sh), 1187(w), 1172(w), 1152(w), 1099(m), 1091(sh), 1070(w), 1030(w), 1015(w), 873(m), 824(w), 809(w), 798(w), 757(sh), 750(sh), 743(vs), 692(s), 669(w), 621(m), 560(w), 528(vs) and 501(m).

^{1}H NMR ($CDCl_3$, ppm): δ = 8.08(t, 1H, 9.1Hz), 7.93 – 7.83(m, 4H), 7.77 – 7.56(m, 5H), 7.56 – 7.36(m, 13H), 7.25 – 7.12(m, 2H), 7.06 – 6.93(m, 2H) and 2.28(s, 3H).

^{31}P NMR ($CDCl_3$-d$_6$): δ = 26.27 ppm.

^{13}C NMR spectrum of **4** was not recorded due to its low solubility in deuterated solvents.

4.4 Preparation of complexes 7–10

Compound *mer*-[Re(*p*-NTol)X$_3$(PPh$_3$)$_2$] (0.54 mmol) was added to the corresponding phenolate-based ligand (0.60 mmol) in methanol (60 mL) and the reaction mixture was refluxed for 4 h. The resulting solution was allowed to evaporate slowly at room temperature. A brown crystalline precipitate of **7–10** was filtered off and dried in the air. X-ray quality brown crystals of **7–9** were obtained by slow recrystallization from methanol.

[Re(*p*-NTol)Cl(L^1)(PPh$_3$)$_2$]·ReO$_4$ (7). (0.43 g of [Re(*p*-NTol)Cl$_3$(PPh$_3$)$_2$] and 0.13 g of 2-(2-hydroxy-5-methylphenyl)benzotriazole yielded to 370 mg of **7**; yield 60%). $C_{56}H_{47}ClN_4O_5P_2Re_2$ (1325.77): calcd. C 50.73, H3.57, N 4.23 %; found C 50.91, H 3.44, N 4.39 %. IR (KBr; ν/cm^{-1}): 3052(w), 1590(w), 1572(w), 1503(m), 1497(sh), 1481(w), 1435(m), 1335(w), 1300(w), 1264(w), 1251(sh), 1212(w), 1195(w), 1176(w), 1161(w), 1133(w), 1091(m), 1071(sh), 1021(w), 997(w), 973(w), 905(vs), 837(m), 824(sh), 802(w), 786(w), 745(s), 693(s), 651(sh), 638(w), 615(w), 558(w), 537(sh), 518(sh), 512(s), 496(sh), 485(sh) and 447(w).

^{1}H NMR (DMSO, ppm): δ = 7.91(d, 1H, 8.7Hz), 7.63(t, 1H, 7.4Hz), 7.38-7.28(m, 8H), 7.25-7.15(m, 25H), 7.11-7.05(m, 2H), 6.90(d, 2H, 8.2Hz), 6.68(d, 2H, 8.2Hz), 2.31(s, 3H), 2.16(s, 3H).

^{13}C NMR (125 MHz, DMSO-d$_6$): δ = 151.0, 148.6, 148.4, 143.7, 143.6, 142.4, 142.3, 133.7, 133.6, 133.3, 132.5, 131.9, 131.5, 129.7, 129.1, 129.0, 128.0, 127.8, 127.7, 127.4, 124.5, 122.3, 121.9, 120.1, 118.4, 118.2, 115.7, 20.5, 20.4 ppm.

^{31}P NMR (DMSO-d$_6$): δ = 25.76 ppm.

[Re(*p*-NTol)Br(L^1)(PPh$_3$)$_2$]ReO$_4$ (8). (0.52 g of [Re(*p*-NTol)Br$_3$(PPh$_3$)$_2$] and 0.13 g of 2-(2-hydroxy-5-methylphenyl)benzotriazole yielded to 410 mg of **8**; yield 60%). $C_{56}H_{49}BrN_4O_6P_2Re_2$ (1388.24): calcd. C 48.45, H 3.56, N 4.04 %; found C 48.64, H 3.61, N 4.12 %. IR (KBr; ν/cm^{-1}): 3053(w), 1590(w), 1571(sh), 1503(m), 1496(m), 1481(sh), 1434(m), 1334(w), 1310(w), 1298(w), 1264(m), 1251(sh), 1209(w), 1196(w), 1176(w), 1160(w), 1135(w), 1090(m), 1072(sh), 1018(w), 997(w), 908(vs), 904(vs), 836(m), 824(sh), 785(w), 763(sh), 743(s), 694(s), 651(w), 638(w), 614(m), 568(sh), 558(w), 536(sh), 528(sh) 518(s), 512(sh), 496(sh), 487(sh), 474(sh), 458(w) and 446(w).
^{1}H NMR (CDCl$_3$, ppm): δ = 7.91(d, 1H, 8.6Hz), 7.67 – 7.61(m, 1H), 7.42 – 7.31(m, 8H), 7.27 – 7.09(m, 27H), 6.87(d, 2H, 8.2Hz), 6.65(d, 2H, 8.2Hz), 2.32(s, 3H) and 2.17(s, 3H).
^{13}C NMR (125 MHz, DMSO-d$_6$): δ = 151.0, 148.0, 143.9, 142.4, 142.3, 133.8, 133.7, 133.1, 132.5, 131.6, 131.0, 129.8, 129.3, 129.2, 129.0, 128.3, 128.0, 127.9, 127.2, 125.9, 122.3, 120.3, 115.6, 22.1, 20.5.
^{31}P NMR (CDCl$_3$-d$_6$): δ = 25.71 ppm.

[Re(*p*-NTol)Cl(L^2)(PPh$_3$)$_2$]·ReO$_4$ (9). (0.43 g of [Re(*p*-NTol)Cl$_3$(PPh$_3$)$_2$] and 0.14 g of 2-(2-hydroxyphenyl)benzothiazole yielded to 370 mg of **9**; yield 60%). $C_{56}H_{45}ClN_2O_5P_2SRe_2$ (1327.79): calcd. C 50.65, H 3.42, N 2.11 %; found C 50.82, H 3.35, N 2.18 %.
IR (KBr; ν/cm^{-1}): 3058(w), 1622(w), 1589(m), 1559(w), 1482(s), 1458(sh), 1438(m), 1406(w), 1315(m), 1271(m), 1251(m), 1220(m), 1165(sh), 1151(w), 1129(w), 1091(w), 1033(w), 973(m), 933(w), 903(w), 871(sh), 860(w), 817(m), 756(sh), 742(vs), 733(sh), 726(sh), 699(sh), 661(w), 624(w), 518(w), 496(w), 456(w).
^{1}H NMR (CDCl$_3$, ppm): δ = 8.15(d, 1H, 8.7Hz), 8.06(d, 1H, 7.3Hz), 7.74(d, 1H, 8.0Hz), 7.50(dd, 4H, 29.1, 21.6Hz), 7.39 –7.12(m, 30H), 7.11 – 6.99(m, 2H), 6.89(s, 2H), 6.75(d, 1H, 7.3Hz), 2.30(s, 3H).
^{13}C NMR (125 MHz, CDCl$_3$): δ = 165.8, 165.7, 156.8, 151.9, 143.7, 132.9, 132.0, 129.3, 129.0, 126.9, 125.6, 122.6, 122.5, 120.2, 118.8, 117.5 ppm
^{31}P NMR (CDCl$_3$-d$_6$): δ = 25.60 ppm.

[Re(*p*-NTol)Br(L^2)(PPh$_3$)$_2$]ReO$_4$·PPh$_3$ (10). (0.52 g of [Re(*p*-NTol)Br$_3$(PPh$_3$)$_2$] and 0.14 g of 2-(2-hydroxyphenyl)benzothiazole yielded 520 mg of **10**; yield 65%). $C_{74}H_{60}BrN_2O_5P_3SRe_2$ (1634.52): calcd. C 54.38, H 3.70, N 1.71 %; found C 54.61, H 3.79, N 1.65 %.
IR (KBr; ν/cm^{-1}): 3050(w), 1593(w), 1570(sh), 1560(w), 1481(sh), 1469(m), 1443(sh), 1433(m), 1407(w), 1342(w), 1326(w), 1284(w), 1268(w), 1226(w), 1189(w), 1173(w), 1161(w), 1132(w), 1117(w), 1091(m), 1070(w), 1028(w), 1018(w), 997(w), 961(w), 909(vs), 893(s), 848(m), 830(w), 811(w), 766(sh), 743(m), 694(vs), 669(sh), 662(sh), 627(m), 572(w), 559(w), 545(w), 519(s), 493(m), 449(w), 434(w).

^{1}H NMR ($CDCl_3$, ppm): δ = 8.06(d, 1H, 8.3Hz), 7.78(d, 1H, 8.5Hz), 7.52(t, 1H, 7.5Hz), 7.39(d, 10H, 12.7Hz), 7.33(t, 8H, 7.3Hz), 7.24(d, 20H, 1.8Hz), 7.17(t, 13H, 7.4Hz), 6.92 – 6.84(m, 2H), 6.74(d, 1H, 8.2Hz) and 2.31(s, 3H).
^{13}C NMR (125 MHz, DMSO-d_6): δ = 167.8, 162.0, 157.5, 150.5, 149.9, 137.0, 133.8, 133.6, 131.9, 131.5, 129.5, 129.3, 129.2, 128.9, 126.7 123.9, 123.4, 122.9, 121.7, 121.1, 120.2, 22.07 ppm.
^{31}P NMR ($CDCl_3$-d_6): δ = 25.78, -6.76 ppm.

4.5 Preparation of complexes 11–16

Compound *mer*-[Re(*p*-NTol)$X_3(PPh_3)_2$] (0.54 mmol) was added to the corresponding phenolate-based ligand (0.60 mmol) in methanol (60 mL) and the reaction mixture was refluxed for 3 h. After that, the solution of NH_4PF_6 (0.19 g, 1.20 mmol) in methanol (5mL) was added and the reaction mixture was refluxed for one hour. The resulting solution was reduced in volume to 10 mL and allowed to cool to room temperature. A brown crystalline precipitate of **11–16** was filtered off and dried in the air. X-ray quality brown crystals were obtained by slow recrystallization from methanol.

[Re(*p*-NTol)Cl(L^1)$(PPh_3)_2$]·PF_6 (11). (0.43 g of [Re(*p*-NTol)$Cl_3(PPh_3)_2$] and 0.13 g of 2-(2-hydroxy-5-methylphenyl)benzotriazole yielded to 495 mg of **11**; yield 75%). $C_{56}H_{47}ClF_6N_4OP_3Re$ (1220.59): calcd. C 55.11, H 3.88, N 4.59 %; found C 55.37, H 3.94, N 4.46 %. IR (KBr; ν/cm^{-1}): 3332(w), 3060(w), 1591(w), 1571(w), 1498(m),m 1481(w), 1434(m), 1350(w), 1334(w), 1299(w), 1265(w), 1252(w), 1210(w), 1188(w), 1176(w), 1160(w), 1140(w), 1118(w), 1091(w), 1071(w), 1028(w), 1017(w), 998(w), 905(w), 858(sh), 837(vs), 785(w), 743(m), 693(s), 651(w), 639(w), 615(w), 557(m), 529(sh), 519(s), 512(sh), 496(w), 482(w), 447(w).
^{1}H NMR (DMSO-d_6, ppm): δ = 7.91(d, 1H, 8.6Hz), 7.62(t, 3H, 9.1Hz), 7.45-7.28(m, 10H), 7.27-7.14(m, 23H), 6.90(d, 2H, 8.2Hz), 6.68(d, 2H, 8.1Hz), 2.16(s, 3H), 2.09(s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.0, 158.7, 158.5, 155.0, 153.2, 150.9, 149.9, 143.7, 143.2, 140.5, 134.3, 133.8, 133.6, 133.0, 131.9, 131.6, 130.0, 129.6, 129.4, 128.5, 125.6, 122.7, 122.8, 119.9, 116.7, 115.5, 22.3, 20.5 ppm
^{31}P NMR ($CDCl_3$-d_6): δ = 25.63, -144.20 ppm.

[Re(*p*-NTol)Br(L^1)$(PPh_3)_2$]·PF_6 (12). (0.52 g of [Re(*p*-NTol)$Br_3(PPh_3)_2$] and 0.13 g of 2-(2-hydroxy-5-methylphenyl)benzotriazole yielded to 480 mg of **12**; yield 70%).$C_{56}H_{47}BrF_6N_4OP_3Re$ (1265.04): calcd. C 53.17, H 3.74, N 4.43 %; found C 53.41, H 3.81, N 4.57 %. IR (KBr; ν/cm^{-1}): 3060(w), 1591(w), 1571(w), 1503(sh), 1497(m), 1481(w), 1434(m), 1350(w), 1334(w), 1311(w), 1299(w), 1284(w), 1265(w), 1252(w), 1210(w), 1189(w), 1176(w), 1161(w), 1140(w), 1119(w), 1090(w),

1073(w), 1028(w), 1017(w), 998(w), 985(w), 905(w) 859(sh), 836(vs), 785(w), 742(m), 694(m), 651(w), 638(w), 614(w), 557(m), 529(w), 519(m), 512(sh), 497(w), 446(w).

^{1}H NMR (DMSO-d_6, ppm): δ = 7.91(d, 1H, 8.6Hz), 7.64(t, 1H, 7.5Hz), 7.36(dd, 8H, 17.2, 10.0Hz), 7.27-7.10(m, 27H), 6.87(d, 2H, 8.2Hz), 6.66(d, 2H, 8.1Hz),

^{13}C NMR (125 MHz, DMSO-d_6): δ = 152.9, 151.0, 148.0, 143.8, 142.3, 134.2, 133.7, 133.1, 132.5, 131.6, 131.1, 129.7, 129.1, 128.8, 128.3, 128.0, 127.9, 127.1, 125.9, 122.4, 122.2, 120.3, 116.2, 22.1, 20.5 ppm.

^{31}P NMR (DMSO-d_6): δ = 25.61, -144.28 ppm.

[Re(*p*-NTol)Cl(L^2)(PPh$_3$)$_2$]$^{\cdot}$PF$_6$ (13). (0.43 g of [Re(*p*-NTol)Cl$_3$(PPh$_3$)$_2$] and 0.14 g of 2-(2-hydroxyphenyl)benzothiazole yielded to 500 mg of **13**; yield 80%). $C_{56}H_{45}ClF_6N_2OP_3ReS$ (1222.56): calcd. C 55.01, H 3.71, N 2.29 %; found C 55.39, H 3.80, N 2.36 %. IR (KBr; ν/cm^{-1}): 3058(w), 1622(w), 1591(w), 1560(w), 1482(sh), 1472(m), 1458(sh), 1435(m), 1406(w), 1340(w), 1316(w), 1289(w), 1272(w), 1251(w), 1214(w), 1188(w), 1178(w), 1156(w), 1129(w), 1095(w), 1030(w), 1014(w), 998(w), 973(w), 878(sh), 839(vs), 745(s), 726(sh), 695(s), 623(w), 556(w), 521(s), 511(sh), 494(sh), 456(w).

^{1}H NMR (DMSO-d_6, ppm): δ = 8.17(dd, 1H, 12.4, 8.0Hz), 8.07(d, 1H, 8.1Hz), 7.75(d, 1H, 8.7Hz), 7.37-7.12(m, 34H), 6.88(dd, 3H, 16.8, 7.4Hz), 6.75(d, 2H, 8.2Hz), 2.08(s, 3H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 165.8, 165.7, 156.7, 151.8, 134.6, 132.9, 132.0, 131.9, 129.3, 129.2, 128.9, 126.9, 125.6, 122.6, 122.5, 120.2, 118.7, 117.4, 21.2 ppm.

^{31}P NMR (DMSO-d_6): δ = 25.78, -144.15 ppm.

[Re(*p*-NTol)Br(L^2)(PPh$_3$)$_2$]$^{\cdot}$PF$_6$ (14). (0.52 g of [Re(*p*-NTol)Br$_3$(PPh$_3$)$_2$] and 0.14 g of 2-(2-hydroxyphenyl)benzothiazole yielded to 500 mg of **14**; yield 80%). $C_{56}H_{45}BrF_6N_2OP_3ReS$ (1267.02): calcd. C 53.08, H 3.58, N 2.21 %; found C 53.34, H 3.63, N 2.43 %. IR (KBr; ν/cm^{-1}): 3075(sh), 3056(w), 1591(w), 1572(sh), 1560(sh), 1482(sh), 1471(m), 1458(sh), 1442(m), 1436(m), 1405(w), 1378(w), 1339(m), 1329(sh), 1288w), 1273(w), 1226(w), 1213(w), 1191(w), 1178(w), 1155(w), 1128(w), 1097(w), 1089(w), 1071(w), 1028(w), 1013(w), 998(w), 939(w), 903(w), 878(sh), 838(s), 744(m), 726(sh), 696(m), 661(w), 653(w), 622(w), 573(w), 556(m), 521(m), 511(sh), 493(w), 435(w).

^{1}H NMR ($CDCl_3$, ppm): δ = 8.07(d, 1H, 7.9Hz), 7.77(t, 1H, 8.9Hz), 7.52(t, 1H, 7.6Hz), 7.40 – 7.29(m, 8H), 7.29 – 7.13(m, 26H), 6.88(dd, 3H, 11.8, 7.9Hz), 6.74(d, 2H, 8.2Hz) and 2.31(s, 3H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 167.8, 157.6, 149.9, 143.5, 133.8, 131.5, 130.9, 129.8, 129.3, 128.9, 128.5, 128.0, 126.2, 123.5, 123.0, 121.8, 121.2, 118.1, 22.1 ppm.

^{31}P NMR ($CDCl_3$-d_6): δ = 25.71, -144.21 ppm.

[Re(*p*-NTol)Cl(L^3)(PPh_3)$_2$]PF_6·PPh_3 (15). (0.43 g of [Re(*p*-NTol)Cl_3(PPh_3)$_2$] and 0.13 g of 22-(2-hydroxyphenyl)benzoxazole yielded to 550 mg of **15**; yield 80%). $C_{74}H_{60}ClF_6N_2O_2P_4Re$ (1468.77): calcd. C 60.51, H 4.12, N 1.91%; found C 60.85, H 4.21, N 1.99 %. IR (KBr; ν/cm^{-1}): 3053(w), 1605(w), 1594(w), 1570(w), 1560(w), 1530(w), 1481(m), 1460(w), 1434(m), 1369(w), 1337(w), 1314(w), 1272(w), 1257(w), 1245(w), 1187(w), 1173(w), 1161(w), 1139(w), 1117(w), 1092(w), 1071(w), 1029(w), 1018(w), 998(w), 974(w), 940(w), 921(w), 878(sh), 839(vs), 814(sh), 776(w), 764(sh), 753(sh), 744(s), 694(s), 674(sh), 626(w), 589(w), 557(m), 520(m), 511(sh), 494(m), 448(w), 435(w), 416(w).
^{1}H NMR ($CDCl_3$, ppm): δ = 7.74(d, 1H, 8.4Hz), 7.56(t, 1H, 7.5Hz), 7.40(d, 9H, 1.3Hz), 7.35(t, 7H, 7.8Hz), 7.31 – 7.14(m, 34H), 6.93(t, 3H, 8.8Hz), 6.76(d, 2H, 8.2Hz) and 2.34(s, 3H).
^{13}C NMR (125 MHz, DMSO-d_6): δ = 163.7, 160.8, 156.5, 155.0, 154.9, 153.8, 147.2, 145.8, 144.4, 142.0, 133.7, 132.5, 132.8, 131.9, 129.7, 128.2, 119.9, 118.5, 112.7, 112.3, 22.1 ppm.
^{31}P NMR ($CDCl_3$-d_6): δ = 25.85, -6.82, -144.21 ppm.

[Re(*p*-NTol)Br(L^2)(PPh_3)$_2$]PF_6·PPh_3 (16). (0.52 g of [Re(*p*-NTol)Br_3(PPh_3)$_2$] and 0.13 g of 2-(2-hydroxyphenyl)benzoxazole yielded to 560 mg of **16**; yield 75%). $C_{74}H_{60}BrF_6N_2O_2P_4Re$ (1513.23): calcd. C 58.73, H 4.00, N 1.85 %; found C 58.94, H 3.89, N 1.78 %. IR (KBr; ν/cm^{-1}): 3073(sh), 3053(w), 1605(w), 1594(w), 1570(w), 1560(w), 1530(w), 1481(m), 1460(w), 1434(m), 1369(w), 1342(w), 1313(w), 1272(w), 1257(w), 1245(w), 1188(w), 1173(w), 1139(w), 1092(w), 1072(sh), 1028(w), 1017(w), 998(w), 974(w), 940(w), 921(w), 878(sh), 839(vs), 813(sh), 776(w), 763(sh), 753(sh), 744(s), 694(s), 674(sh), 651(w), 625(w), 589(w), 557(m), 520(m), 511(sh), 494(w), 447(w), 436(w), 419(w).
^{1}H NMR ($CDCl_3$, ppm): δ = 7.59(dd, 2H, 17.9, 9.6Hz), 7.40(s, 7H), 7.35(t, 6H, 7.4Hz), 7.22(dt, 33H, 14.7, 9.8Hz), 7.11(s, 3H), 7.05 – 6.87(m, 5H), 6.72(d, 1H, 8.4) and 2.34(s, 3H).
^{13}C NMR (125 MHz, DMSO-d_6): δ = 162.9, 160.9, 152.7, 148.3, 142.2, 133.9, 133.5, 132.7, 132.5, 131.9, 129.3, 129.2, 128.9, 120.9, 119.9, 118.3, 112.6, 22.0 ppm
^{31}P NMR ($CDCl_3$-d_6): δ = 25.74, -6.83, -144.21 ppm.

4.6 Catalytic oxidation of alcohols and alkanes

Catalysts were introduced into the reaction solution in acetonitrile containing a substrate and TBHP. The reactions were typically carried out in air in thermostated Pyrex cylindrical vessels with vigorous stirring; total volume of the reaction solution was 2–5 mL. (**Caution**: the combination of air or molecular oxygen and peroxides with organic compounds at elevated temperatures may be explosive!) Samples of the reaction mixture were taken after certain time intervals, and concentrations of acetophenone were measured using ^{1}H NMR method (Bruker AMX-400 instrument, 400 MHz). Added to the sample

acetone-d_6 was used as a component of the solvent (in addition to acetonitrile); 1,4-dinitrobenzene was a standard. The detection and quantification of the obtained products of the catalytic reactions were made by measuring the areas of peaks corresponding to methyl group from acetophenone (2.6 ppm). Products obtained from octanols and alkanes were analyzed using GC method (chromatograph-3700, fused silica capillary column FFAP/OV-101 20/80 w/w, 30 m × 0.2 mm × 0.3 μm; helium as a carrier gas). The reaction sample was treated with PPh_3 before the analysis.

Conflict of interest

The authors declare no financial interest.

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Graph. Abstr.:

Text:

The reactions of *mer*-[Re(*p*-NTol)$X_3(PPh_3)_2$] (X= Cl, Br) with chelating phenolate-based ligands gave 16 various new *p*-tolylimido rhenium(V) complexes. Interestingly, only a few of them exhibited high catalytic activity in oxidation of alcohols with *tert*-butyl hydroperoxide (TBHP).