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p-Tolylimido rhenium(V) complexes – Synthesis, X-ray studies, spectroscopic characterization and DFT calculations

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ABSTRACT

The p-tolylimido rhenium(V) complexes $[Re(p-NC_6H_4CH_3)X_3(EPh_3)_2]$ (X = Cl, Br; E = As, P) and $[Re(p-NC_6H_4CH_3)Cl_2(hmpbta)(PPh_3)]$ ·MeCN have been synthesized and characterized spectroscopically and structurally. The electronic spectra of $[Re(p-NC_6H_4CH_3)Cl_3(PPh_3)_2]$ and $[Re(p-NC_6H_4CH_3)Cl_2-(hmpbta)(PPh_3)]$ (Hhmpbta-2-(2'-hydroxy-5'-methylphenyl)benzotriazole) were investigated at the TDDFT level employing B3LYP functional in combination with LANL2DZ. Additional information about bonding between the rhenium atom and p-tolylimido ligand in the complexes $[Re(p-NC_6H_4CH_3)Cl_3-(PPh_3)_2]$ and $[Re(p-NC_6H_4CH_3)Cl_2(hmpbta)(PPh_3)]$ was obtained by NBO analysis.

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1. Introduction

Imido complexes are known for the majority of the d-block metals, and they are in the center of scientific interest in context of basic research and employment of them in catalysis. These compounds have been successfully employed in the catalytic hydroamination of alkynes, the synthesis of various nitrogen heterocycles, alkene metathesis, activation of hydrocarbons including methane, and in cycloaddition reactions with unsaturated organic substrates [1–6].

The properties of the metal-nitrogen bond can vary greatly with differences in the steric and electronic environment, and the coordinated imido ligand can adopt a variety of geometries: terminal linear (A), terminal bent (B), doubly bridging (C) and triply bridging (D) [1–6].



A thorough understanding of bonding between transition metals and imido ligands is of great theoretical and commercial interest.

Recently, high-valent imido complexes of Tc and Re have been also proposed as potential radiopharmaceuticals as alternatives to oxo and nitrido compounds owing to the possibility of incorpo-

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rating specific targeting molecules on the substituents at the nitrogen site. Although kit preparations for the imaging of almost all main organs and organ systems exist and there is some experience in the labeling of biomolecules, there is still a need for new approaches and new labeling procedures. It is obvious that promising contributions are expected from the coordination chemistry and organometallic chemistry which plays an important role in the development of novel rhenium and technetium radiopharmaceuticals. It is a challenge for synthetic chemists to supply novel methods and compound for the radiopharmaceutical community [7].

In this context, the design, synthesis and reactivity of novel imido rhenium complexes has become the aim of several laboratories, including ours.

The first arylimido rhenium complexes were synthesized by Chatt and Rowe in 1962 using aniline as the source of the imido ligand. The analogous [Re(NAr)X₃(PPh₃)₂] compounds were subsequently reported [8–22], but surprisingly, only few of them were structurally examined, namely [Re(NC₆H₅)Cl₃(PPh₃)₂]·CH₂Cl₂ [12] [Re(NC₆H₅)Cl₃(PPh₃)₂]·CHCl₃ [13], [Re(NC₆H₅)Cl₂(OMe)(PPh₃)₂]. CH₂Cl₂ [14], [Re(o-NC₆H₄NHCH₃)Br₂Cl(PPh₃)₂] [15], [Re(o,o-NC₆H₄(OH)(NH₂)Cl₃(PPh₃)₂] [16], [Re(o-NC₆H₄NHPh)Cl₃(PPh₃)₂]. CH₂Cl₂ [17], [Re(p-NC₆H₄COONC₄H₄O₂)Cl₃(PPh₃)₂]·CH₂Cl₂·EtOH [18], [Re(m-NC₆H₄COCH₃)Cl₃(PPh₃)₂]·(CH₃)₂CO [19], [Re(o-NC₆-H₄NH₂)Cl₃(PPh₃)₂] [20], [Re(p-NC₆H₄(CH₂)₃COOEt)Cl₃(PPh₃)₂] [21], [Re(p-NC₆H₄NH₂)Cl₃(PPh₃)₂] ·PPh₃ [22]. Although the complex [Re(p-NC₆H₄CH₃)Cl₃(PPh₃)₂] has been known and used as starting material in the synthesis of arylimido rhenium complexes, its crystal and molecular structure has not been determined so far.

In the first step of our studies we have structurally characterized the imido Re(V) complexes $[Re(p-NC_6H_4CH_3)X_3(PPh_3)_2]$





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Scheme 1. Structure of Hhmpbta ligand.

(X = Cl, Br), as well as we have synthesized and examined their arsine analogues $[Re(p-NC_6H_4CH_3)X_3(AsPh_3)_2]$ for the first time.

The second step of our study has concerned the reactivity of $[\text{Re}(p-\text{NC}_6\text{H}_4\text{CH}_3)\text{Cl}_3(\text{PPh}_3)_2]$ towards 2-(2'-hydroxy-5'-methylphenyl)benzotriazole (Hhmpbta, see Scheme 1).

Recently some oxo rhenium complexes incorporating this ligand have been synthesized and characterized [23], but imido transition metal compounds of 2-(2'-hydroxy-5'-methylphenyl)benzotriazole are unknown. Furthermore, to our best knowledge only two other transition metal complexes with hmpbta⁻ ion are structurally characterized so far – [MoO₂(a-cac)(hmpbta)] and [{VO(acac)₂}(μ -L)] (acac – acetylacetonate). In the Mo complex the 2-(2'-hydroxy-5'-methylphenyl)benzotriazolate ion is coordinated in a bidentate mode, whereas in the V oxo-complex – as bridging ligand [24].

The experimental studies on the imido rhenium complexes have been accompanied computationally by the density functional theory (DFT) and time-dependent DFT calculations. Currently density functional theory (DFT) is commonly used to examine the electronic structure of transition metal complexes. It meets with the requirements of being accurate, easy to use and fast enough to allow the study of relatively large molecules of transition metal complexes [25,26].

Additional information about bonding between the rhenium atom and imido ligand in $[Re(p-NC_6H_4CH_3)Cl_3(PPh_3)_2]$ and $[Re(p-NC_6H_4CH_3)Cl_2(hmpbta)(PPh_3)]$ has been obtained by NBO analysis.

2. Experimental

2.1. General procedure

The syntheses of $[\text{Re}(\text{p-NC}_6\text{H}_4\text{CH}_3)X_3(\text{AsPh}_3)_2]$ were carried out under argon atmosphere. The solvents were of reagent grade and used as received. Ammonium perrhenate, triphenylphosphine, triphenylarsine and p-toluidine were purchased from Aldrich. The complexes $[\text{ReOX}_3(\text{EPh}_3)_2]$ (X = Cl, Br; E = As, P) and $[\text{Re}(\text{p-NC}_6\text{H}_4\text{CH}_3)X_3(\text{PPh}_3)_2]$ were prepared according to the literature methods [27,9].

Infrared spectra were recorded on a Nicolet Magna 560 spectrophotometer in the spectral range $4000 \div 400 \text{ cm}^{-1}$ with the samples in the form of potassium bromide pellets. Electronic spectra were measured on a spectrophotometer Lab Alliance UV–Vis 8500 in the range $1100 \div 180 \text{ nm}$ in deoxygenated acetonitrile solution. ¹H NMR spectrum was obtained in CDCl₃ using Bruker Avance 400 spectrometer. Elemental analysis (C H N) was performed on a Perkin-Elmer CHN-2400 analyzer.

2.2. $[Re(p-NC_6H_4CH_3)Cl_3(PPh_3)_2]$ (1)

IR (KBr; v/cm^{-1}): 3060 (m), 1590 (m), 1572 (w), 1483 (m), 1434 (s), 1338 (w), 1310 (w), 1198 (w), 1170 (w), 1089 (m), 1016 (w), 822 (m), 745 (m), 694 (s), 561 (w), 521 (s), 509 (s), 494(m), 458 (w) and 444(w).

¹H NMR (CDCl₃, ppm): δ = 7.96–7.88 (m, 10H), 7.26–7.21 (m, 20H), 6.69 (t, 2H) 6.48 (t, 2H) 2.11 (s, 3H).

Anal. Calc. for C₄₃H₃₇Cl₃P₂NRe: C, 56.00; H, 4.04; N, 1.52. Found: C, 50.64; H, 3.97; N, 1.63%.

2.3. $[Re(p-NC_6H_4CH_3)Br_3(PPh_3)_2]$ (2)

IR (KBr; v/cm⁻¹): 3016 (m), 1591 (m), 1481 (m), 1434 (s), 1389 (w), 1340 (w), 1306 (w), 1196 (w), 1174 (w), 1096 (m), 1029 (w), 824 (m), 744 (m), 709 (sh), 693 (s), 564 (w), 522 (s), 512 (sh), 500 (sh), 449 (w).

UV–Vis (CH₃CN; λ_{max} [nm] (ε; [dm³ mol⁻¹ cm⁻¹])): 712.6 (250), 344.3 (14450), 255.3 (38650), 222.2 (179100).

Anal. Calc. for C₄₃H₃₇Br₃P₂NRe: C, 48.93; H, 3.53; N, 1.33. Found: C, 48.85; H, 3.55; N, 1.48%.

2.4. Preparation of $[Re(p-NC_6H_4CH_3)Cl_3(AsPh_3)_2]$ (3)

trans-[ReOCl₃(AsPh₃)₂] (0.5 g, 0.54 mmol) and p-toluidine (0.85 g, 0.79 mmol) in benzene (100 ml) was refluxed for 6 h under argon atmosphere. The resulting solution was reduced in volume to ~10 ml, and green crystalline precipitate of **3** was filtered off and dried in the air. X-ray quality crystals were obtained by recrystallization from acetonitrile. Yield 60%.

IR (KBr; v/cm⁻¹): 3056 (m), 1590 (m), 1571 (sh), 1483 (m), 1435 (s), 1338 (w), 1310 (w), 1189 (w), 1169 (w), 1076 (m), 1025 (w), 823 (m), 738 (m), 692 (s), 559 (w), 472 (s) and 457(sh), 444(w).

UV–Vis (CH₃CN; λ_{max} [nm] (ϵ ; [dm³ mol⁻¹ cm⁻¹])): 759.4 (130), 342.0 (16530), 245.0 (64800), 220.4 (120790).

Anal. Calc. for $C_{43}H_{37}Cl_3As_2NRe: C, 51.13$; H, 3.69; N, 1.39. Found: C, 51.63; H, 3.57; N, 1.43%.

2.5. Preparation of $[Re(p-NC_6H_4CH_3)Br_3(AsPh_3)_2]$ (4)

A procedure similar to that for **3** was used with *trans*-[ReO-Br₃(AsPh₃)₂] (0.50 g, 0.47 mmol) and p-toluidine (0.80, 0.75 mmol). Yield 55%.

IR (KBr; ν /cm⁻¹): 3054 (w), 1591 (m), 1572 (sh), 1482 (m), 1434 (s), 1361 (w) 1337 (w), 1301 (w), 1186 (m), 1169 (m), 1114 (m), 1074 (m), 1024 (w), 821 (s), 736 (s), 692 (s), 648 (w), 616 (w), 561 (m), 475 (s) and 453(m), 444(w).

UV–Vis (CH₃CN; λ_{max} [nm] (ε; [dm³ mol⁻¹ cm⁻¹])): 632.3 (375), 344.6 (24760), 240.0 (84620), 220.7 (180590).

Anal. Calc. for C₄₃H₃₇Br₃As₂NRe: C, 45.16; H, 3.26; N, 1.22. Found: C, 45.40; H, 3.36; N, 1.29%.

2.6. Preparation of [Re(p-NC₆H₄CH₃)Cl₂(hmpbta)(PPh₃)₂]·MeCN (**5**·MeCN)

 $[{\rm Re}(p-{\rm NC}_6{\rm H_4}{\rm CH_3}){\rm Cl}_3({\rm PPh}_3)_2]$ (0.50 g, 0.54 mmol) was added to 2-(2'-hydroxy-5'-methylphenyl)benzotriazole (0.14 g, 0.62 mmol) in acetonitrile (50 ml) and the reaction mixture was refluxed for 5 h. The resulting solution was reduced in volume to ${\sim}10$ ml and allowed to cool to room temperature. A green crystalline precipitate of **5**-MeCN was filtered off and dried in the air. X-ray quality crystals were obtained by recrystallization from acetonitrile Yield 80%.

IR (KBr; v/cm⁻¹): 3049 (w), 1590 (m), 1570 (w), 1482 (m), 1433 (s), 1355 (w), 1317 (w), 1187 (m), 1169 (m), 1089 (m), 1017 (m), 819 (m), 744 (s), 694 (s), 619(w), 561 (m), 520 (s), 497 (s), 453 (m) and 418(w).

¹H NMR (CDCl₃, ppm): δ = 7.94 (d,1H), 7.88 (d,1H), 7.54 (t,1H), 7.32–7.20 (m,10H), 7.12–7.05 (m,6H), 7.16 (t,1H), 6.96 (d,2H), 6.88 (d,1H), 6.81 (d,3H), 2.28 (s,3H), 2.03 (s,3H).

Anal. Calc. for $C_{40}H_{35}PCl_2N_5ORe:$ C, 53.99; H, 3.96; N, 7.87. Found: C, 54.25; H, 3.89; N, 7.98%.

2.7. Crystal structures determination and refinement

The X-ray intensity data of **1–5** were collected on a Gemini A Ultra diffractometer equipped with Atlas CCD detector and graphite monochromated Mo K α radiation (λ = 0.71073 Å) 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 [28] were applied. The structures were solved by the Patterson method and subsequently completed by the difference Fourier recycling. 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. SHELXS 97 and SHELXL 97 [29] programs were used for all the calculations. Atomic scattering factors were those incorporated in the computer programs.

2.8. Computational details

The gas phase geometries of **1** and **5** were optimised without any symmetry restrictions in singlet ground-states with the DFT method using the hybrid B3LYP functional of GAUSSIAN 03 [30–32]. The calculations were performed using ECP LANL2DZ basis set [33] with an additional *d* and *f* function with the exponent $\alpha = 0.3811$ and 2.033 [34] for the rhenium and the standard 6-31G basis set for the other atoms. For chlorine, oxygen, nitrogen and phosphorous atoms, diffuse and polarization functions were added [35]. All vibrations in the calculated vibrational spectrum of **1** and **5** were real, thus the both geometries correspond to true energy minimum.

The electronic spectra of **1** and **5** were calculated with the TDDFT method [36], and the solvent effect (acetonitrile) was simulated using the polarizable continuum model with the integral

Table 1

Crystal data and structure refinement for 1, 2, 3, 4 and 5 MeCN.

equation formalism (IEF-PCM) [37]. For complexes **1** and **5**, 120 and 110 singlet–singlet spin-allowed excitations in solution were taken into account, respectively.

Natural bond orbital (NBO) calculations were performed with the NBO code [38] included in GAUSSIAN 03.

3. Results and discussion

3.1. Synthesis

The diamagnetic complexes $[\text{Re}(p-\text{NC}_6\text{H}_4\text{CH}_3)X_3(\text{EPh}_3)_2]$ (X = Cl, Br; E = As, P) have been prepared in good yield by a standard method – in the reactions of *trans*- $[\text{ReOX}_3(\text{EPh}_3)_2]$ with an excess of ptoluidine in benzene

 $[\text{ReOX}_3(\text{EPh}_3)_2] + p - H_2\text{N} - C_6H_4 - CH_3 \rightarrow [\text{Re}(p - 1)_3] + p - H_2\text{N} - C_6H_4 - CH_3 \rightarrow [\text{Re}(p - 1)_3] + p - H_2\text{N} - C_6H_4 - CH_3 \rightarrow [\text{Re}(p - 1)_3] + p - H_2\text{N} - C_6H_4 - CH_3 \rightarrow [\text{Re}(p - 1)_3] + p - H_2\text{N} - C_6H_4 - CH_3 \rightarrow [\text{Re}(p - 1)_3] + p - H_2\text{N} - C_6H_4 - CH_3 \rightarrow [\text{Re}(p - 1)_3] + p - H_2\text{N} - C_6H_4 - CH_3 \rightarrow [\text{Re}(p - 1)_3] + p - H_2\text{N} - C_6H_4 - CH_3 \rightarrow [\text{Re}(p - 1)_3] + p - H_2\text{N} - C_6H_4 - CH_3 \rightarrow [\text{Re}(p - 1)_3] + p - H_2\text{N} - C_6H_4 - CH_3 \rightarrow [\text{Re}(p - 1)_3] + p - H_2\text{N} - C_6H_4 - CH_3 \rightarrow [\text{Re}(p - 1)_3] + p - H_2\text{N} - C_6H_4 - CH_3 \rightarrow [\text{Re}(p - 1)_3] + p - H_2\text{N} - C_6H_4 - CH_3 \rightarrow [\text{Re}(p - 1)_3] + p - H_2\text{N} - C_6H_4 - CH_3 \rightarrow [\text{Re}(p - 1)_3] + p - H_2\text{N} - C_6H_4 - CH_3 \rightarrow [\text{Re}(p - 1)_3] + p - H_2\text{N} - C_6H_4 - CH_3 \rightarrow [\text{Re}(p - 1)_3] + p - H_2\text{N} - C_6H_4 - CH_3 \rightarrow [\text{Re}(p - 1)_3] + p - H_2\text{N} - C_6H_4 - CH_3 \rightarrow [\text{Re}(p - 1)_3] + p - H_2\text{N} - C_6H_4 - CH_3 \rightarrow [\text{Re}(p - 1)_3] + p - H_2\text{N} - C_6H_4 - CH_3 \rightarrow [\text{Re}(p - 1)_3] + p - H_2\text{N} - C_6H_4 - CH_3 \rightarrow [\text{Re}(p - 1)_3] + p - H_2\text{N} - C_6H_4 - CH_3 \rightarrow [\text{Re}(p - 1)_3] + p - H_2\text{N} - C_6H_4 - CH_3 \rightarrow [\text{Re}(p - 1)_3] + p - H_2\text{N} - C_6H_4 - CH_3 \rightarrow [\text{Re}(p - 1)_3] + p - H_2\text{N} - C_6H_4 - CH_3 \rightarrow [\text{Re}(p - 1)_3] + p - H_2\text{N} - C_6H_4 - CH_3 \rightarrow [\text{Re}(p - 1)_3] + p - H_2\text{N} - C_6H_4 - CH_3 \rightarrow [\text{Re}(p - 1)_3] + p - H_2\text{N} - C_6H_4 - CH_3 \rightarrow [\text{Re}(p - 1)_3] + p - H_2\text{N} - C_6H_4 - CH_3 \rightarrow [\text{Re}(p - 1)_3] + p - H_2\text{N} - C_6H_4 - CH_3 \rightarrow [\text{Re}(p - 1)_3] + p - H_2\text{N} - C_6H_4 - CH_3 \rightarrow [\text{Re}(p - 1)_3] + p - H_2\text{N} - C_6H_4 - CH_3 \rightarrow [\text{Re}(p - 1)_3] + p - H_2\text{N} - C_6H_4 - CH_3 \rightarrow [\text{Re}(p - 1)_3] + p - H_2\text{N} - C_6H_4 - CH_3 \rightarrow [\text{Re}(p - 1)_3] + p - H_2\text{N} - C_6H_4 - CH_3 \rightarrow [\text{Re}(p - 1)_3] + p - H_2\text{N} - C_6H_4 - CH_3 \rightarrow [\text{Re}(p - 1)_3] + p - H_2\text{N} - C_6H_4 - CH_3 \rightarrow [\text{Re}(p - 1)_3] + p - H_2\text{N} - C_6H_4 - CH_3 \rightarrow [\text{Re}(p - 1)_3] + p - H_2\text{N} - C_6H_4 - CH_3 \rightarrow [\text{Re}(p - 1)_3] + p - H_2\text{N} - CH_3 - CH_3 \rightarrow [\text{Re}(p - 1)_3] + p - H_2\text{N} - CH_3 - CH_3 \rightarrow [\text{Re}(p - 1)_3] + p - H_2\text{N} -$

 $NC_6H_4CH_3X_3(EPh_3)_2$] + H_2O (X = Cl, Br; E = P, As).

Since the complexes $[ReOX_3(AsPh_3)_2]$ easily transform into $[ReOX_3(AsPh_3)(OAsPh_3)]$ in solution in air [39], the syntheses of $[Re(p-NC_6H_4CH_3)X_3(AsPh_3)_2]$ were carried out under argon atmosphere.

The substitution reaction of $[\text{Re}(p-\text{NC}_6\text{H}_4\text{CH}_3)\text{Cl}_3(\text{PPh}_3)_2]$ with 2-(2'-hydroxy-5'-methylphenyl)benzotriazole (Hhmpbta) leads to the formation of the neutral imido compound $[\text{Re}(p-\text{NC}_6\text{H}_4\text{CH}_3)\text{Cl}_2(\text{hmpbta})(\text{PPh}_3)]$ -MeCN.

All the complexes **1–5** are formally rhenium(V) compounds with the p-tolylimido unit as a dianionic NR^{2-} ligand. Since the imido core NR^{2-} is isoelectronic to the core O^{2-} and tends to form analogous complexes with rhenium, a short comparison with the Re(V) oxocompounds deserves comment.

The $[ReOX_3(EPh_3)_2]$ (X = Cl, Br; E = P, As) complexes are convenient starting materials. In the reactions with uninegative N,O-donor chelate ligand they form mono- and di-substituted compounds of $[ReOX_2(N-O)(EPh_3)]$ and $[ReOX(N-O)_2]$ type [23,40–46]. The

	1	2	3	4	5·MeCN
Empirical formula	C ₄₃ H ₃₇ Cl ₃ P ₂ NRe	C ₄₃ H ₃₇ Br ₃ P ₂ NRe	C ₄₃ H ₃₇ Cl ₃ As ₂ NRe	C ₄₃ H ₃₇ Br ₃ As ₂ NRe	C ₄₀ H ₃₅ Cl ₂ N ₅ OPRe
Formula weight	922.23	1055.61	1010.13	1143.51	889.80
Temperature (K)	293(2)	293(2)	293(2)	293.0(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Space group	$P2_{a}/c$	$P2_n/n$	$P2_{1/c}$	$P2_n/n$	
Unit cell dimensions	121/0	121/11	121/0	121/1	P1
a (Å)	14.4134(2)	12.5079(2)	14.3802(2)	12.650(3)	10.610(2)
b (Å)	10.8466(17)	14.0679(2)	10.9126(2)	14.089(3)	12.830(3)
c (Å)	24.3129(4)	22.5556(3)	24.7596(3)	22.661(5)	14.498(3)
α (°)	-	-	-	90	92.07(3)
β (°)	97.106(17)	101.786(2)	96.239(2)	100.77(3)	104.89(3)
γ (°)	-	-	-	90	103.04(3)
Volume (Å ³)	3771.8(6)	3885.21(10)	3862.4(10)	3967.6(14)	1848.8(6)
Z	4	4	4	4	2
$D_{calc} (Mg m^{-3})$	1.624	1.805	1.737	1.914	1.598
Absorption coefficient (mm ⁻¹)	3.552	6.327	5.086	7.771	3.513
F(0 0 0)	1832	2048	1976	2192	884
Crystal size (mm)	$0.166 \times 0.120 \times 0.070$	$0.158\times0.157\times0.007$	$0.225 \times 0.106 \times 0.101$	$0.228\times0.201\times0.114$	$0.102 \times 0.118 \times 0.08$
θ Range for data collection (°)	3.38-25.00	3.33-25.00	3.43-25.00	3.44-25.00	3.39-25.00
Index ranges	$-17 \leq h \leq 16$ $-12 \leq k \leq 12$	$-14 \leqslant h \leqslant 14$ $-16 \leqslant k \leqslant 16$	$-17 \le h \le 17$ $-12 \le k \le 12$	$-15 \le h \le 15$ $-16 \le k \le 16$	$-12 \leqslant h \leqslant 12$ $-15 \leqslant k \leqslant 15$
Reflections collected	–28 ≤ l ≤ 28	–26 ≤ <i>l</i> ≤ 26	–29 <i>≤ l ≤</i> 29	–26 <i>≤ l ≤</i> 26	$-17 \leqslant l \leqslant 17$
	35 792	37 667	37 903	37 152	34 860
Independent reflections (R_{int})	6622 (0.0323)	6828 (0.0271)	6785 (0.0270)	6966 (0.0407)	6510 (0.0255)
Completeness to $2\theta = 25^{\circ}$ (%)	99.8	99.8	99.8	99.7	99.8
Minimum and maximum transmission	0.635–1.000	0.475–1.000	0.522-1.000	0.387–1.000	0.853-1.000
Data/restraints/parameters	6622/0/452	6828/0/452	6785/0/452	6966/0/452	6510/0/454
Goodness-of-fit (GOF) on F^2	0.966	0.942	1.011	1.027	1.011
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0176$	$R_1 = 0.0183$	$R_1 = 0.0210$	$R_1 = 0.0256$	$R_1 = 0.0180$
R indices (all data)	$w_{R_2} = 0.0377$	$w_{R_2} = 0.0398$	$w_{R_2} = 0.0452$	$w_{R_2} = 0.0559$	$w_{R_2} = 0.0426$
	$R_1 = 0.0244$	$R_1 = 0.0292$	$R_1 = 0.0291$	$R_1 = 0.0457$	$R_1 = 0.0224$
	$w_{R_2} = 0.0386$	$w_{R_2} = 0.041$	$w_{R_2} = 0.0464$	$w_{R_2} = 0.0591$	$w_{R_2} = 0.0432$
Largest difference peak and hole [e $Å^{-3}$]	0.488 and -0.426	0.504 and -0.556	0.732 and -0.473	0.623 and -0.766	0.735 and -0.331

course of these reactions depends on many factors, including type of the ligand and reaction conditions. The title 2-(2'-hydroxy-5'-methylphenyl)benzotriazole (Hhmpbta) reacts with [ReOX₃-(EPh₃)₂] complexes to give monosubstituted [ReOX₂(hmpb-ta)(EPh₃)]·MeCN stereoisomers with *cis* halide arrangement [23].

The imido rhenium complexes incorporating uninegative N,Odonor chelate ligands have been studied relatively rarely [47,48]. The [Re(p-NC₆H₄CH₃)X₃(EPh₃)₂] complexes are supposed to react in similar way to the analogous [ReOX₃(EPh₃)₂]. The examined reaction of [Re(p-NC₆H₄CH₃)Cl₃(PPh₃)₂] with 2-(2'-hydroxy-5'-methylphenyl)benzotriazole (Hhmpbta) seems to support this hypothesis. Likewise as [ReOCl₃(PPh₃)₂], the [Re(p-NC₆H₄CH₃)Cl₃(PPh₃)₂] complex reacts with Hhmpbta to give *cis*-[Re(p-NC₆H₄CH₃)Cl₂(hmpbta)(PPh₃)]·MeCN. Surprisingly, the *cis*-X,X arrangement in the [Re(NAr)X₂(N-O)(PPh₃)] complexes has not been confirmed so far [47], whereas the majority of the known [ReOX₂(O–N)(PPh₃)] structures has halide ligands in *cis* geometry [23,40–46].

Similar to the related imido complexes it is extremely difficult to identify the Re-NC₆H₄CH₃ stretches in the IR spectra of **1–5**, as they may be mixed with $v_{C=N}$ and v_{P-C} modes of PPh₃ and hmpbta⁻ ligands [8–22]. The experimental vibrational spectra of **1** and **5** are compared to the calculated (non-scaled) ones (Figs. 1 and 2). For both complexes the calculated $v(\text{Re-NC}_6\text{H}_4\text{CH}_3)$ frequencies appear at ~1425 and 1050 cm⁻¹.

In the ¹H NMR spectra of **1** and **5** the aromatic region containing signals from protons of the phenyl groups of the imido and triphenylphosphine molecules (8.00–6.40 ppm) is accompanied by distinctive signals corresponding the alkyl protons of p-methylphenylimido and hmpbta[–] ligands (2.30–2.00 ppm). The ¹H NMR spectrum of **1** measured in CDCl₃ shows the phenyl-imido resonances as a two triplets at 6.69 and 6.48 ppm, methyl-imido resonances as a singlet at 2.11 ppm and phenyl proton of the coordinated PPh₃ molecules as two multiplets in the ranges 7.96–7.88 and 7.26–7.21 ppm. The ¹H NMR spectrum of **5** shows

the methyl groups of the hmpbta[–] and imido ligands as singlets at 2.28 and 2.03 ppm. The aromatic region of the ¹H NMR spectrum is more difficult to identify, owing to some overlapping of the signals of the aromatic protons of phosphine, organoimido and hmpbta[–] ligands. However, the phenyl proton of the coordinated PPh₃ molecule appear as two multiplets in the ranges 7.32–7.20 and 7.12–7.05 ppm. The benzotriazole protons appear in the range 7.12–7.05 and downfield as three singlets at 7.94, 7.88, 7.54 ppm. The protons of the phenyl-imido and phenyl-subsituent of benzotriazole ring (in hmpbta[–] ligand) fall upfield as doublets and triplets in the range 7.16–6.80 ppm. In the both spectra of **1** and **5** there is no evidence of paramagnetic broadening, confirming that complexes [Re(p-NC₆H₄NH₂)Cl₃(PPh₃)₂] and [Re(p-NC₆H₄CH₃)Cl₂-(hmpbta)(PPh₃)]·MeCN are diamagnetic.

3.2. X-ray studies

The crystallographic data of **1–4** and **5**·MeCN are summarized in Table 1. The short intra- and intermolecular contacts detected in the imido complexes are gathered in Table 2. In the structures $[Re(p-NC_6H_4CH_3)X_3(EPh_3)_2]$ (X = Cl, Br; E = As, P) and $[Re(p-NC_6H_4CH_3)Cl_2(hmpbta)(PPh_3)]$ ·MeCN the classical hydrogen bonds can not be found, only some C-H···X, C-H···O and C-H···N weak inter- and intramolecular hydrogen bonds exist [49,50].

3.3. $[Re(p-NC_6H_4CH_3)X_3(EPh_3)_2]$ complexes

All the complexes $[\text{Re}(p-\text{NC}_6\text{H}_4\text{CH}_3)X_3(\text{EPh}_3)_2]$ show octahedral geometry about the central rhenium atom defined by the p-methylphenylimido group, three halide ions in *meridional* geometry and the two mutually *trans*-triphenylphosphine or triphenylarsine molecules. The ligands *cis* to the p-methylphenylimido group are all bowed slightly away from p-NC₆H₄CH₃ moiety to minimize steric congestion around the rhenium atom.



Fig. 1. The experimental and calculated (non-scaled) vibrational spectra of 1.



Fig. 2. The experimental and calculated (non-scaled) vibrational spectra of 5.

 Table 2

 Short intra- and intermolecular contacts detected in 1-4 and 5-MeCN

$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	144.8
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	146.1
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	148.9
C30-H30···Cl30.932.66 $3.380(3)$ 2 $(S^{-}+HS\cdots Br^{2})$ 0.932.88 $3.679(3)$ C14-H14···Br20.932.88 $3.751(3)$ C20-H20···Br20.932.82 $3.562(3)$ 3 $(S^{-}+HS\cdots Cl2)$ C8-H8···Cl30.932.71 $3.448(4)$ 220 -H20···Cl20.932.81 $3.435(4)$ C8-H8···Cl30.932.71 $3.448(4)$ 220 -H20···Cl20.932.67 $3.493(4)$ C28-H28···Cl2_#20.932.82 $3.592(4)$ $C33$ -H33···Cl1_#34 $C26$ -H26···Br20.935-MeCN $S6$ -H(s) 0.02 2.44 C6-H(s) 0.02 2.44 $2.327(4)$	124.5
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	135.0
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	144.7
C20-H20···Br2 0.93 2.82 $3.562(3)$ 35 C8-H8···Cl2 0.93 2.81 $3.435(4)$ C8-H8···Cl3 0.93 2.71 $3.448(4)$ C20-H20···Cl2 0.93 2.67 $3.493(4)$ C28-H28···Cl2_#2 0.93 2.82 $3.592(4)$ C33-H33···Cl1_#3 0.93 2.71 $3.512(4)$ 4CCC 0.93 2.89 $3.679(5)$ 5 ·MeCN 5 ·MeCN 5 ·MeCN 5 ·MeCN	155.7
3	138.1
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	
$C8-H8\cdots CI3$ 0.93 2.71 $3.448(4)$ $C20-H20\cdots CI2$ 0.93 2.67 $3.493(4)$ $C28-H28\cdots CI2_\#2$ 0.93 2.82 $3.592(4)$ $C33-H33\cdots CI1_\#3$ 0.93 2.71 $3.512(4)$ 4 C26-H26\cdots Br2 0.93 2.89 $3.679(5)$ 5 ·MeCN C6 100 0.02 2.44 $2.327(4)$	125.9
$C20-H20\cdots Cl2$ 0.93 2.67 $3.493(4)$ $C28-H28\cdots Cl2_#2$ 0.93 2.82 $3.592(4)$ $C33-H33\cdots Cl1_#3$ 0.93 2.71 $3.512(4)$ 4 $C6-H26\cdots Br2$ 0.93 2.89 $3.679(5)$ 5 ·MeCN $C6-H26\cdots 01$ 0.023 2.44 $2.327(4)$	137.0
C28-H28···Cl2_#2 0.93 2.82 3.592(4) C33-H33···Cl1_#3 0.93 2.71 3.512(4) 4 C26-H26···Br2 0.93 2.89 3.679(5) 5-MeCN C6 UC 0.02 2.44 2.327(4)	148.1
C33-H33···Cl1_#3 0.93 2.71 3.512(4) 4 C26-H26···Br2 0.93 2.89 3.679(5) 5-MeCN C6 UC 01 0.02 2.44 2.327(4)	141.2
4 C26-H26···Br2 0.93 2.89 3.679(5) 5 -MeCN C6 U(C 01 0.02 2.44 2.327(4)	144.7
C26-H26···Br2 0.93 2.89 3.679(5) 5·MeCN	
5-MeCN	142.9
CC UC 01 0.02 2.44 2.227(4)	
0.93 2.44 3.237(4)	143.2
C27-H27N1 0.93 2.61 3.168(3)	118.7
C30-H30Cl2_#2 0.93 2.78 3.631(3)	152.2
C37-H37…N4 0.93 2.43 2.746(4)	99.7

#1: -*x*, 1-*y*, 1-*z*; #2: 1-*x*, 2-*y*, 1-*z*; #3: -*x*, 1-*y*, 1-*z*.



The Re(1)–N(1)–C(37) bond angles in the structures [Re(p-NC₆H₄CH₃)X₃(EPh₃)₂] [170.32(17)° for **1**, 176.87(19)° for **2** and 169.4(2)° for **3** and 176.8(3)° for **4**] agree with the linear coordination mode of the arylimido ligands. The Re–N(1) bond lengths of [Re(p-NC₆H₄CH₃)X₃(EPh₃)₂] [1.7113(19) Å for **1**, 1.710(2) Å for **2**



Fig. 3. The molecular structure of 1. Displacement ellipsoids are drawn at 50% probability.

and 1.726(3) Å for **3** and 1.707(3) Å for **4**] fall in the range 1.67– 1.74 Å, typical of mononuclear complexes of rhenium(V) having $[Re = NR]^{3+}$ core, and indicate the presence of a triple bond Re = N[8-22]. These values are in good agreement with those for *mer, trans*- $[Re(NPh)Cl_3(PPh_3)_2]$ (1.726(6) Å and 172.6(6)°) and $[Re(4-NC_6H_4NH_2)Cl_3(PPh_3)_2]$ (1.719(4) Å and 177.2(4)°) [12,22].

Table	3
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The experimental and optimised bond lengths (Å) and angles (°) for 1.

Bond lengths	Experimental	Optimised	Bond angles	Experimental	Optimised
Re(1)-N(1)	1.7173(19)	1.713	N(1)-Re(1)-Cl(1)	96.17(6)	90.59
Re(1)-Cl(1)	2.3973(7)	2.489	N(1)-Re(1)-Cl(2)	174.04(6)	176.35
Re(1)-Cl(2)	2.4102(6)	2.477	Cl(1)-Re(1)-Cl(2)	89.79(2)	90.59
Re(1)-Cl(3)	2.4398(7)	2.515	N(1)-Re(1)-Cl(3)	87.82(6)	89.28
Re(1)-P(1)	2.4936(6)	2.558	Cl(1)-Re(1)-Cl(3)	176.00(2)	177.48
Re(1)-P(2)	2.4871(6)	2.545	Cl(2)-Re(1)-Cl(3)	86.22(2)	87.25
			N(1)-Re(1)-P(1)	97.11(6)	96.04
			Cl(1)-Re(1)-P(1)	87.40(2)	90.19
			Cl(2)-Re(1)-P(1)	83.14(3)	84.99
			Cl(3)-Re(1)-P(1)	92.41(2)	88.31
			N(1)-Re(1)-P(2)	94.13(6)	95.98
			Cl(1)-Re(1)-P(2)	89.25(2)	89.07
			Cl(2)-Re(1)-P(2)	85.90(3)	83.01
			Cl(3)-Re(1)-P(2)	90.17(2)	91.97
			P(1)-Re(1)-P(2)	168.55(2)	167.97
			Re(1)-N(1)-C(37)		175.34

Table 4	
The experimental bond lengths (A	Å) and angles (°) for 2 , 3 , 4 complexes.

Bond lengths	2 X = Br	3 X = CI: E = As	4 X = Br: E = As	Bond angles	2 X = Br	3 X = CI: E = As	4 X = Br: E = As
Re(1)-N(1) Re(1)-X(1) Re(1)-X(2) Re(1)-X(3) Re(1)-E(1) Re(1)-E(2)	1.710(2) 2.5595(3) 2.5832(3) 2.5730(3) 2.5005(7) 2.4859(7)	1.726(3) 2.3920(8) 2.4080(8) 2.4327(8) 2.5569(3) 2.5612(3)	1.707(3) 2.5681(7) 2.5755(8) 2.5582(6 2.5546(10) 2.5551(10)	$\begin{array}{c} N(1)-Re(1)-X(1)\\ N(1)-Re(1)-X(2)\\ X(1)-Re(1)-X(2)\\ N(1)-Re(1)-X(3)\\ X(3)-Re(1)-X(1)\\ X(3)-Re(1)-X(2)\\ N(1)-Re(1)-E(1)\\ E(1)-Re(1)-E(1)\\ E(1)-Re(1)-X(2)\\ E(1)-Re(1)-X(2)\\ E(1)-Re(1)-X(2)\\ E(2)-Re(1)-X(3)\\ N(1)-Re(1)-X(2)\\ E(2)-Re(1)-X(3)\\ E(2)-Re(1)-X(3)\\ E(1)-Re(1)-E(2)\\ Re(1)-R(1)-E(2)\\ Re(1)-N(1)-C(37)\\ \end{array}$	92.26(6) 176.01(7) 90.617(9) 90.69(6) 176.769(10) 86.500(9) 90.82(7) 89.271(17) 91.99(2) 89.371(17) 90.94(7) 88.353(16) 86.376(18) 92.916(17) 177.10(2) 176.87(19)	96.20(8) 175.18(8) 88.47(3) 88.78(8) 174.95(3) 86.57(3) 93.52(8) 90.20(2) 85.25(2) 90.30(2) 97.32(8) 87.21(2) 84.07(2) 91.37(2) 169.065(11) 169.4(2)	$\begin{array}{c} 91.41(10)\\ 177.68(10)\\ 86.883(14)\\ 92.30(10)\\ 176.242(15)\\ 89.420(15)\\ 90.45(10)\\ 89.507(13)\\ 91.10(2)\\ 89.892(13)\\ 91.11(10)\\ 92.541(13)\\ 87.40(2)\\ 87.960(13)\\ 177.392(14)\\ 176.8(3) \end{array}$

The Re–P and Re–Cl bond distances fall within the normal range in six-coordinate rhenium complexes [12–22].

3.4. $cis-[Re(p-NC_6H_4CH_3)Cl_2(hmpbta)(PPh_3)]$ ·MeCN complex

The perspective drawing of $[Re(p-NC_6H_4CH_3)Cl_2-$ (hmpbta)(PPh₃)] MeCN is presented in Fig. 4, and the selected bond distances and angles of 5 MeCN are collected in Table 5. The rhenium atom is coordinated by p-methylphenylimido group, two chloride ions, the phosphorus atom of PPh₃ molecule and the bidentate N,O donor of the 2-(2'-hydroxy-5'-methylphenyl)benzotriazolato ligand. The oxygen atom of 2-(2'-hydroxy-5'-methylphenyl)benzotriazolato ligand occupies trans position to the 4methylphenylimido ion and triphenylphosphine molecule with their π -acidity adopts *cis* position with respect to the RN \equiv Re–O unit. Consequently, the RN=Re-O core with multiply bonded imido ligand is stabilized to some extent due to accessible π -donation from rhenium to triphenylphosphine molecule.

The chloride ions of **5**·MeCN are arranged in *cis* geometry, similar as in the related [ReOCl₂(hmpbta)(PPh₃)]·MeCN. The majority of the known [ReOX₂(O–N)(PPh₃)] structures has halide ligands in *cis* geometry [23,40–46], whereas the *cis*-X,X arrangement in the [Re(NAr)X₂(N–O)(PPh₃)] complexes has been confirmed for the first time. The chloride ions of the known [Re(p-NC₆H₄CH₃) Cl₂(RN=CHC₆H₄O)(PPh₃)] (R = Ph, Me) occupy trans positions to each other [47].

The Re(1) atom of **5** MeCN is displaced 0.1569(6) Å from the plane formed by the two halogen, one nitrogen and one phospho-

rous atoms (plane A), 0.0401(8) Å from the plane formed by the two nitrogen, one halogen and oxygen atoms (plane B) and 0.0065(7) Å from the plane formed by nitrogen, oxygen, halogen and phosphorous atoms (plane C). Least squares plane A is inclined at 89.25(5)° to plane B and at 88.90(5)° to plane C; planes B and C are inclined at 87.49(5)°, respectively.

The interatomic distance between the rhenium atom and the oxygen atom of hmpbta⁻ ligand is shorter than an ideal single Re–O bond length (*ca.* 2.04 Å) [51], indicating small delocalization in the N(1)–Re(1)–O(1) moiety. The Re–N(1) bond length of [Re(p-NC₆H₄CH₃)Cl₂(hmpbta)(PPh₃)]·MeCN [1.720(2) Å] falls in the range 1.67–1.74 Å, typical of mononuclear complexes of rhenium(V) having [Re \equiv NR]³⁺ core, and indicate the presence of a triple bond Re \equiv N [8–22]. The Re(1)–N(1)–C(19) bond angle in the structure [Re(p-NC₆H₄CH₃)Cl₃(PPh₃)₂] [175.99(18)°] agrees with the linear coordination mode of the p-NC₆H₄CH₃ ligand [52–54].

The elongation of the Re(1)-Cl(2) distance *trans* to the phosphorus atom of PPh₃ molecule in comparison with Re(1)-Cl(1) bond *trans* to the nitrogen atom of the 2-(2'-hydroxy-5'-methylphenyl)benzotriazolato ligand in **5**·MeCN is a consequence of *structural trans* effect of the PPh₃ ligand.

3.5. Geometry optimisation, charge distribution, electronic structure and NBO analysis

The geometries of the complexes **1** and **5** were optimised in singlet states using the DFT method with the B3LYP functional. The optimised geometric parameters are gathered in Tables 3 and 5.



Fig. 4. The molecular structure of 5-MeCN. Displacement ellipsoids are drawn at 50% probability.

The calculated bond lengths and angles are in agreement with the values based upon the X-ray crystal structure data, and the general trends observed in the experimental data are well reproduced in the calculations.

Table 6 presents the atomic charges from the Natural Population Analysis (NPA) for **1** and **5**. The calculated charge on the rhenium atom in **5** is larger in comparison with the starting compound $[\text{Re}(\text{p-NC}_6\text{H}_4\text{CH}_3)\text{Cl}_3(\text{PPh}_3)_2]$ (**1**). However, the both values are considerably lower than the formal charge +5. The populations of the d_{xy} , d_{xz} , d_{yz} , $d_{x^2-y^2}$ and d_{z^2} rhenium orbitals are following: 1.078, 1.949, 0.911, 1.146 and 1.046 for **1** and 1.004, 1.036, 1.050, 1.223 and 1.485 for **5**. It confirms significant charge donation from the NR²⁻ and hmpbta⁻ ligands, chloride ions and triphenylphosphine molecule.

The $[\text{Re}(p-\text{NC}_6\text{H}_4\text{CH}_3)\text{Cl}_3(\text{PPh}_3)_2]$ and $[\text{Re}(p-\text{NC}_6\text{H}_4\text{CH}_3)\text{Cl}_2-(\text{hmpbta})(\text{PPh}_3)]$ are closed-shell structures. Their partial molecular orbital diagrams with the several highest occupied and lowest unoccupied molecular orbital contours are presented in Figs. 5

 Table 5

 The experimental and optimised bond lengths [Å] and angles [°] for 5-MeCN.

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Atomic charges from the Natural Population Analysis (NPA) for $[Re(p-NC_6H_4CH_3)Cl_3(PPh_3)_2]$ (1) and $[Re(p-NC_6H_4CH_3)Cl_2(hmpbta)(PPh_3)]$ (5).

Atom	1	5
Re(1)	-0.554	0.773
Cl(1)	-0.315	-0.429
Cl(2)	-0.292	-0.464
Cl(3)	-0.337	
P(1)	1.528	1.384
P(2)	1.535	
N(1)	-0.161	-0.315
O(1)		-0.689
N(2)		-0.278

and 6, respectively. In discussion of the orbital character the local symmetry of the rhenium center has been considered; for complex **1**: *z*-axis goes along the N(1)-Re–Cl(2) linkage, and *x*-axis – through the P(1)-Re–P(2) bonds; for complex **5**: *z*-axis goes along the N(1)-Re–O(1) linkage, and *x*-axis – through the P(1)-Re–Cl(2) bonds.

The highest occupied MO of **1** is of rhenium d_{xy} type with an antibonding contribution from p_{π} chloride orbitals. The d_{yz} , d_{xy} , d_{z^2} and $d_{x^2-y^2}$ orbitals of the central atom constitute mainly the LUMO, LUMO+1, LUMO+2 and LUMO+3, respectively. The d_{yz} and d_{xy} rhenium orbitals bear antibonding character towards the p_{π} nitrogen orbitals of the imido ligand; the LUMO, LUMO+1 can be considered as $\pi^*_{Re} \equiv_{NR}$ orbitals. The value of the energy separation between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) equals to 2.99 eV.

The HOMO and HOMO-1 of **5** are of d_{xy} type with some contributions from p_{π} chloride and hmpbta⁻ orbitals. The LUMO and LUMO+1 can be ascribed as π -antibonding rhenium–imido molecular orbitals. The $d_{x^2-y^2}$ and d_{z^2} rhenium orbital contributes to the LUMO+3 and LUMO+8, respectively. The value of the energy separation between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of **5** equals to 3.13 eV. This value is considerable higher in comparison with the HOMO–LUMO gap of **1** being the starting material in the synthesis of [Re(p-NC₆H₄CH₃)Cl₂(hmpbta)(PPh₃)]. The bigger absolute value of the energy gap means better stability, and explains easily formation of **5** in the reaction of **1** with 2-(2'-hydroxy-5'-methylphenyl)benzotriazole. On the other hand the complex **5** seems to be only more stable than the related oxocompound [ReOCl₂(hmpbta)] with HOMO–LUMO gap equal to 3.10 eV [23].

The nature of the rhenium-imido ligand interaction in **1** and **5** has been studied by NBO analysis. The occupancy and composition of the calculated Re–NR natural bond orbitals (NBOs) are given in Table 7.

Experimental	Optimised	Bond angles	Experimental	Optimised
1.720(2)	1.724	N(1)-Re(1)-O(1)	172.58(8)	173.49
1.9881(17)	2.022	N(1)-Re(1)-N(2)	93.14(9)	97.30
2.140(2)	2.151	O(1)-Re(1)-N(2)	80.68(7)	80.95
2.3744(9)	2.452	N(1)-Re(1)-Cl(1)	97.28(7)	94.13
2.4560(13)	2.529	O(1)-Re(1)-Cl(1)	89.36(6)	88.41
2.4319(13)	2.471	N(2)-Re(1)-Cl(1)	167.56(6)	166.70
		N(1)-Re(1)-P(1)	90.36(7)	90.64
		O(1)-Re(1)-P(1)	86.52(6)	83.41
		N(2)-Re(1)-P(1)	98.47(6)	97.62
		Cl(1)-Re(1)-P(1)	88.28(3)	89.00
		N(1)-Re(1)-Cl(2)	95.24(7)	94.13
		O(1)-Re(1)-Cl(2)	88.37(6)	89.39
		N(2)-Re(1)-Cl(2)	85.27(6)	83.49
		Cl(1)-Re(1)-Cl(2)	87.01(4)	88.48
		Cl(2)-Re(1)-P(1)	173.09(2)	172.44
		Re(1)-N(1)-C(19)	175.99(18)	173.30
	Experimental 1.720(2) 1.9881(17) 2.140(2) 2.3744(9) 2.4560(13) 2.4319(13)	Experimental Optimised 1.720(2) 1.724 1.9881(17) 2.022 2.140(2) 2.151 2.3744(9) 2.452 2.4560(13) 2.529 2.4319(13) 2.471	Experimental Optimised Bond angles 1.720(2) 1.724 N(1)-Re(1)-O(1) 1.9881(17) 2.022 N(1)-Re(1)-N(2) 2.140(2) 2.151 O(1)-Re(1)-N(2) 2.3744(9) 2.452 N(1)-Re(1)-Cl(1) 2.4560(13) 2.529 O(1)-Re(1)-Cl(1) 2.4319(13) 2.471 N(2)-Re(1)-Cl(1) N(1)-Re(1)-P(1) N(1)-Re(1)-P(1) N(1)-Re(1)-P(1) O(1)-Re(1)-P(1) N(2)-Re(1)-Cl(2) O(1)-Re(1)-Cl(2) O(1)-Re(1)-Cl(2) O(1)-Re(1)-Cl(2) O(1)-Re(1)-Cl(2) O(1)-Re(1)-Cl(2) O(1)-Re(1)-Cl(2) O(1)-Re(1)-Cl(2) O(1)-Re(1)-Cl(2) Cl(1)-Re(1)-Cl(2) Cl(1)-Re(1)-Cl(2) O(1)-Re(1)-Cl(2) Cl(2)-Re(1)-Cl(2) Cl(2)-Re(1)-Cl(2) O(1)-Re(1)-Cl(2) Cl(2)-Re(1)-Cl(2) Cl(2)-Re(1)-Cl(2) O(1)-Re(1)-Cl(2) Cl(2)-Re(1)-Cl(2) Cl(2)-Re(1)-Cl(2) O(1)-Re(1)-Cl(2) Cl(2)-Re(1)-Cl(2) Cl(2)-Re(1)-Cl(2)	$\begin{tabular}{ c c c c c c } \hline Experimental & Optimised & Bond angles & Experimental \\ \hline Experimental & Optimised & Bond angles & Experimental \\ \hline 1.720(2) & 1.724 & N(1)-Re(1)-O(1) & 172.58(8) \\ 1.9881(17) & 2.022 & N(1)-Re(1)-N(2) & 93.14(9) \\ 2.140(2) & 2.151 & O(1)-Re(1)-N(2) & 80.68(7) \\ 2.3744(9) & 2.452 & N(1)-Re(1)-Cl(1) & 97.28(7) \\ 2.4560(13) & 2.529 & O(1)-Re(1)-Cl(1) & 89.36(6) \\ 2.4319(13) & 2.471 & N(2)-Re(1)-Cl(1) & 167.56(6) \\ N(1)-Re(1)-P(1) & 90.36(7) \\ O(1)-Re(1)-P(1) & 98.47(6) \\ Cl(1)-Re(1)-P(1) & 98.47(6) \\ Cl(1)-Re(1)-P(1) & 88.28(3) \\ N(1)-Re(1)-Cl(2) & 95.24(7) \\ O(1)-Re(1)-Cl(2) & 88.37(6) \\ N(2)-Re(1)-Cl(2) & 85.27(6) \\ Cl(1)-Re(1)-Cl(2) & 87.01(4) \\ Cl(2)-Re(1)-Cl(2) & 87.01(4) \\ Cl(2)-Re(1)-P(1) & 173.09(2) \\ Re(1)-N(1)-C(19) & 175.99(18) \\ \hline \end{tabular}$



Fig. 5. The energy (eV), character and some contours of the unoccupied molecular orbitals of $[Re(p-NC_6H_4CH_3)Cl_3(PPh_3)_2]$ (1). Positive values of the orbital contour are represented in blue (0.04 au) and negative values – in yellow (-0.04 au). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

In the both imido complexes, three Re–NR natural bond orbitals were detected. The Re–N bond orbital of σ -character is strongly polarized towards the nitrogen atom, and the s and p nitrogen orbitals and s and d rhenium orbitals take part in the bond formation. The Re–N bond orbitals of π -character are result of overlapping of the empty d_{xy} and d_{yz} rhenium orbitals with the occupied p_x and p_z orbitals of the deprotonated nitrogen of the imido ligand.

3.6. Electronic spectra

The experimental and calculated electronic spectra of **1** and **5** are presented in Figs. 7 and 8, respectively. The positions of absorption bands for the other [Re(p-NC₆H₄CH₃)X₃(EPh₃)₂] complexes are given in the experimental part. Each calculated transition for **1** and **5** is represented by a gaussian function $y = ce^{-bx^2}$ with the height (c) equal to the oscillator strength and *b* equal to 0.04 nm⁻².

Tables 8 and 9 present the most important electronic transitions calculated with the TDDFT method assigned to the observed absorption bands of **1** and **5**, respectively. For the high energy part of the spectrum, only transitions with oscillator strengths larger than 0.030 are listed in Tables 8 and 9.

The investigated complexes are of large size; the numbers of basis functions are equal to 838 for **1** and 786 for **6**. The calculated electron transitions do not comprise all the experimental absorption bands. Thus the shortest wavelength experimental bands of the examined complexes are not assigned to the calculated transitions or the assignment is not complete.

The assignment of the calculated orbital excitations to the experimental bands was based on an overview of the contour plots and relative energy to the occupied and unoccupied orbitals involved in the electronic transitions.

3.7. Electronic spectrum of 1

The low-energy absorption band of **1** originates from the HOMO \rightarrow LUMO and HOMO \rightarrow LUMO+1 transitions. As it can be seen from the Fig. 5, the HOMO is composed of p_{π} chloride orbitals and d_{xy} rhenium atomic orbital, the LUMO and LUMO+1 are delocalized on central ion and π -antibonding orbitals of the p-meth-



Fig. 6. The energy (eV), character and some contours of the unoccupied molecular orbitals of [Re(p-NC₆H₄CH₃)Cl₂(hmpbta)(PPh₃)] (**5**). Positive values of the orbital contour are represented in blue (0.04 au) and negative values – in yellow (–0.04 au). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 7

The occupancy and composition of the calculated natural bond orbitals (NBOs) between the rhenium and the p-tolylimido ligand for $[Re(p-NC_6H_4CH_3)Cl_3(PPh_3)_2]$ (1) and $[Re(p-NC_6H_4CH_3)Cl_2(hmpbta)(PPh_3)]$ (5).

Occupancy	Composition of NBO	BD*	Occupancy
1.94	$0.520 (sp^{0.33}d^{2.50})_{Re} + 0.854 (sp^{0.74})_{N}$	$0.854 (sp^{0.33}d^{2.50})_{Re} - 0.520 (sp^{0.74})_{Ne}$	0.23
1.97	0.627 (d) _{Re} + 0.779 (p) _N	0.779 (d) _{Re} – 0.627 (p) _N	0.18
1.90	0.664 (d) _{Re} + 0.748 (p) _N	$0.748 (d)_{Re} - 0.664 (p)_{N}$	0.25
1.96	$0.486 (sp^{0.01}d^{2.90})_{Re} + 0.874(sp^{0.83})_{N}$	$0.874 (sp^{0.01}d^{2.90}) - 0.486 (sp^{0.83})_N$	0.30
1.97	0.629 (d) _{Re} + 0.777 (p) _N	$0.777 (d)_{Re} - 0.629 (p)_{N}$	0.22
1.92	0.656 (d) _{Re} + 0.755 (p) _N	$0.755 (d)_{Re} - 0.656 (p)_{N}$	0.35
	Occupancy 1.94 1.97 1.90 1.96 1.97 1.92	Occupancy Composition of NBO 1.94 $0.520 (sp^{0.33}d^{2.50})_{Re} + 0.854 (sp^{0.74})_{N}$ 1.97 $0.627 (d)_{Re} + 0.779 (p)_{N}$ 1.90 $0.664 (d)_{Re} + 0.748 (p)_{N}$ 1.96 $0.486 (sp^{0.01}d^{2.90})_{Re} + 0.874 (sp^{0.83})_{N}$ 1.97 $0.629 (d)_{Re} + 0.777 (p)_{N}$ 1.92 $0.656 (d)_{Re} + 0.755 (p)_{N}$	$\begin{tabular}{ c c c c c } \hline Occupancy & Composition of NBO & BD^* \\ \hline 1.94 & 0.520 (sp^{0.33} d^{2.50})_{Re} + 0.854 (sp^{0.74})_N & 0.854 (sp^{0.33} d^{2.50})_{Re} - 0.520 (sp^{0.74})_N \\ \hline 1.97 & 0.627 (d)_{Re} + 0.779 (p)_N & 0.779 (d)_{Re} - 0.627 (p)_N \\ \hline 1.90 & 0.664 (d)_{Re} + 0.748 (p)_N & 0.748 (d)_{Re} - 0.664 (p)_N \\ \hline 1.96 & 0.486 (sp^{0.01} d^{2.90})_{Re} + 0.874 (sp^{0.83})_N & 0.874 (sp^{0.01} d^{2.90}) - 0.486 (sp^{0.83})_N \\ \hline 1.97 & 0.629 (d)_{Re} + 0.777 (p)_N & 0.777 (d)_{Re} - 0.629 (p)_N \\ \hline 1.92 & 0.656 (d)_{Re} + 0.755 (p)_N & 0.755 (d)_{Re} - 0.656 (p)_N \\ \hline \end{tabular}$

BD denotes 2-center bond; * denotes antibond NBO.

ylphenylimido ligand. Accordingly, the transition at 716.1 nm can be seen as a delocalized MLLCT (*Metal–Ligand-to-Ligand CT*) transition. However, considering that the molecular orbitals, involved in the electronic transitions assigned to the longest wavelength experimental band, comprise mainly rhenium 5d atomic orbitals (Fig. 3), the HOMO \rightarrow LUMO and HOMO \rightarrow LUMO+1 transitions may be ascribed as transitions of d \rightarrow d character. The transitions assigned to the experimental bands at 344.3 and 253.0 nm can be seen as mixed $\pi(Cl)/\pi(p-tol)/\pi(PPh_3) \rightarrow Re$ (*Ligand–Metal Charge Transfer; LMCT*) and $\pi(Cl)/\pi(p-tol)/\pi(PPh_3) \rightarrow \pi^*(p-tol)$ (*Ligand–Ligand Charge Transfer; LLCT*) transitions.

The absorption band at 221.5 nm results mainly from *Ligand–Ligand Charge Transfer* and interligand (*IL*) transitions.



Fig. 7. The experimental (black) and calculated (red) electronic absorption spectra of $[\text{Re}(\text{p-NC}_6\text{H}_4\text{CH}_3)\text{Cl}_3(\text{PPh}_3)_2]$ (1). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.8. Electronic spectrum of 5

Likewise for 1, the longest wavelength experimental band of 5 may be attributed to the transition of $d \rightarrow d$ character or may be



Fig. 8. The experimental (black) and calculated (red) electronic absorption spectra of $[\text{Re}(p-NC_6H_4CH_3)Cl_2(\text{hmpbta})(\text{PPh}_3)]$ (5). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 8

The energy and molar absorption coefficients of experimental absorption bands and the electronic transitions calculated with the TDDFT method for $[Re(p-NC_6H_4CH_3)Cl_3(PPh_3)_2]$ (1).

The most important orbital excitations	Character	λ (nm)	<i>E</i> (eV)	f	Experimental Λ (nm) (E (eV)) ε
$H \rightarrow L$	$d/\pi(Cl) \rightarrow d/\pi^*(p-tol)$	684.0	1.81	0.0001	716.1 (1.73) 200
$H \rightarrow L+1$	$d/\pi(Cl) \rightarrow d/\pi^*(p-tol)$	648.3	1.91	0.0011	
$H-2 \rightarrow L$	$\pi(p-tol)/d/\pi(Cl) \rightarrow d/\pi^*(p-tol)$	366.7	3.38	0.0906	344.1 (3.60) 13 600
$H-7 \rightarrow L$	$\pi(\text{PPh}_3) \rightarrow d/\pi^*(\text{p-tol})$	354.7	3.50	0.0830	
$H-8 \rightarrow L$	$\pi(\text{PPh}_3)/\pi(\text{p-tol}) \rightarrow d/\pi^*(\text{p-tol})$	347.2	3.57	0.0326	
$H-10 \rightarrow L$	$\pi(\text{PPh}_3) \rightarrow d/\pi^*(\text{p-tol})$	345.9	3.58	0.0300	
$H-11 \rightarrow L$	$\pi(\text{Cl})/\pi(\text{p-tol})/\pi(\text{PPh}_3) \rightarrow d/\pi^*(\text{p-tol})$	332.5	3.73	0.0329	
$H-6 \rightarrow L$	$\pi(\text{PPh}_3) \rightarrow d/\pi^*(\text{p-tol})$				
$H-16 \rightarrow L$	$\pi(\text{Cl})/\pi(\text{p-tol}) \rightarrow d/\pi^*(\text{p-tol})$	306.4	4.05	0.0425	
$H-13 \rightarrow L+1$	$\pi(\text{PPh}_3) \rightarrow d/\pi^*(\text{p-tol})$	302.4	4.10	0.0596	
$H-12 \rightarrow L+1$	$\pi(\text{Cl})/\pi(\text{p-tol})/\pi(\text{PPh}_3) \rightarrow d/\pi^*(\text{p-tol})$				
$H \rightarrow L+5$	$d/\pi(Cl) \rightarrow \pi^*(PPh_3)$	291.4	4.26	0.0405	253.0 (4.90) 28 100
$H-15 \rightarrow L+1$	$\pi(\text{Cl})/\pi(\text{PPh}_3) \rightarrow d/\pi^*(\text{p-tol})$				
$H-1 \rightarrow L+2$	$\pi(\text{Cl})/n(\text{P})/\pi(\text{PPh}_3) \rightarrow d/\pi^*(\text{PPh}_3)$	288.9	4.29	0.2812	
$H-17 \rightarrow L+1$	$\pi(\text{PPh}_3)/\pi(\text{Cl}) \rightarrow d/\pi^*(\text{p-tol})$	283.0	4.38	0.0703	
$H-18 \rightarrow L+1$	$\pi(\text{Cl}) \rightarrow d/\pi^*(\text{p-tol})$	279.0	4.44	0.0605	
$H-19 \rightarrow L$	$\pi(\text{Cl}) \rightarrow d/\pi^*(\text{p-tol})$	268.2	4.62	0.0403	
$H-1 \rightarrow L+3$	$\pi(\text{Cl})/n(\text{P})/\pi(\text{PPh}_3) \rightarrow d/\pi^*(\text{PPh}_3)$	262.9	4.72	0.0821	
$H-4 \rightarrow L+2$	$\pi(\text{PPh}_3) \rightarrow d/\pi^*(\text{PPh}_3)$	257.4	4.82	0.0363	
$H-1 \rightarrow L+4$	$\pi(\text{Cl})/n(\text{P})/\pi(\text{PPh}_3) \rightarrow \pi^*(\text{PPh}_3)$	255.7	4.85	0.0459	
$H-11 \rightarrow L+2$	$\pi(\text{Cl})/\pi(\text{p-tol})/\pi(\text{PPh}_3) \rightarrow d/\pi^*(\text{PPh}_3)$	242.1	5.12	0.0421	
$H-1 \rightarrow L+7$	$\pi(\text{Cl})/n(\text{P})/\pi(\text{PPh}_3) \rightarrow \pi^*(\text{p-tol})/\pi^*(\text{PPh}_3)$				
$H \rightarrow L+13$	$d/\pi(Cl) \rightarrow \pi^*(PPh_3)$	241.9	5.13	0.0459	
$H-1 \rightarrow L+7$	$\pi(\text{Cl})/n(\text{P})/\pi(\text{PPh}_3) \rightarrow \pi^*(\text{p-tol})/\pi^*(\text{PPh}_3)$				
$H-1 \rightarrow L+6$	$\pi(\text{Cl})/n(\text{P})/\pi(\text{PPh}_3) \rightarrow \pi^*(\text{PPh}_3)$				
$H-2 \rightarrow L+4$	$\pi(p-tol)/\pi(Cl)/d \rightarrow \pi^*(PPh_3)$	233.9	5.30	0.0306	221.5 (5.60) 59 040
$H-22 \rightarrow L$	$\sigma(N) \rightarrow d/\pi^*(p-tol)$	232.7	5.33	0.0368	
$H-14 \rightarrow L+2$	$\pi(p-tol) \rightarrow d/\pi^*(PPh_3)$	232.2	5.34	0.0407	
$H-5 \rightarrow L+5$	$\pi(\text{PPh}_3)/\pi(\text{Cl}) \rightarrow \pi^*(\text{PPh}_3)$				
$H-1 \rightarrow L+8$	$\pi(\text{Cl})/n(\text{P})/\pi(\text{PPh}_3) \rightarrow \pi^*(\text{p-tol})/\pi^*(\text{PPh}_3)$				
$H-4 \rightarrow L+5$	$\pi(\text{PPh}_3) \rightarrow \pi^*(\text{PPh}_3)$	228.3	5.43	0.0376	
$H \rightarrow L+17$	$d/\pi(Cl) \rightarrow \pi^*(p-tol)/d$				
$H-10 \rightarrow L+4$	$\pi(\text{PPh}_3) \rightarrow \pi^*(\text{PPh}_3)$	224.5	5.52	0.0354	
$H-11 \rightarrow L+4$	$\pi(\text{Cl})/\pi(\text{p-tol})/\pi(\text{PPh}_3) \rightarrow \pi^*(\text{PPh}_3)$				
$H-11 \rightarrow L+3$	$\pi(\text{Cl})/\pi(\text{p-tol})/\pi(\text{PPh}_3) \rightarrow d/\pi^*(\text{PPh}_3)$				

ε - molar absorption coefficient [dm³ mol⁻¹ cm⁻¹]; f - oscillator strength; H - highest occupied molecular orbital; L - lowest unoccupied molecular orbital.

Table 9

The energy and molar absorption coefficients of experimental absorption bands and the electronic transitions calculated with the TDDFT method for [Re(p-NC₆H₄CH₃)Cl₂(hmpbta)(PPh₃)] (**5**).

The most important orbital excitations	Character	λ (nm)	<i>E</i> (eV)	f	Experimental Λ (nm) (<i>E</i> (eV)) ε
$H \rightarrow L$	$d/\pi(hmpbta)/\pi(Cl) \rightarrow d/\pi^*(p-tol)$	621.9	1.99	0.0055	582.5 (2.13) 300
$H \rightarrow L+1$	$d/\pi(hmpbta)/\pi(Cl) \rightarrow d/\pi^*(hmpbta)/\pi^*(p-tol)$	601.2	2.06	0.0004	. ,
$H \rightarrow L+1$	$d/\pi(hmpbta)/\pi(Cl) \rightarrow d/\pi^*(hmpbta)/\pi^*(p-tol)$	482.1	2.57	0.0426	401.3 (3.10) 14 700
$H-1 \rightarrow L$	$d/\pi(hmpbta)/\pi(Cl) \rightarrow d/\pi^*(p-tol)$	470.1	2.64	0.1082	
$H \rightarrow L+1$	$d/\pi(hmpbta)/\pi(Cl) \rightarrow d/\pi^*(hmpbta)/\pi^*(p-tol)$				
$H \rightarrow L+2$	$d/\pi(hmpbta)/\pi(Cl) \rightarrow d/\pi^*(hmpbta)/\pi^*(p-tol)$	415.7	2.98	0.1624	
$H-1 \rightarrow L+2$	$d/\pi(hmpbta)/\pi(Cl) \rightarrow d/\pi^*(hmpbta)/\pi^*(p-tol)$	391.2	3.17	0.0801	
$H-2 \rightarrow L$	$\pi(p-tol)/\pi(hmpbta)/d \rightarrow d/\pi^*(p-tol)$	365.6	3.39	0.0458	320.0 (3.87) 23 150
$H-4 \rightarrow L$	$\pi(\text{PPh}_3) \rightarrow d/\pi^*(\text{p-tol})$	354.5	3.50	0.0543	
$H-3 \rightarrow L$	$\pi(p-tol)/\pi(hmpbta)/d \rightarrow d/\pi^*(p-tol)$	348.0	3.56	0.0442	
$H-5 \rightarrow L$	$\pi(\text{hmpbta})/d \rightarrow d/\pi^*(\text{p-tol})$	340.8	3.64	0.1997	
$H-4 \rightarrow L+1$	$\pi(\text{PPh}_3) \rightarrow d/\pi^*(\text{hmpbta})/\pi^*(\text{p-tol})$	337.4	3.67	0.0697	
$H-3 \rightarrow L+1$	$\pi(p-tol)/\pi(hmpbta)/d \rightarrow d/\pi^*(hmpbta)/\pi^*(p-tol)$				
$H-7 \rightarrow L$	$\pi(PPh_3) \rightarrow d/\pi^*(p-tol)$	333.0	3.72	0.0666	
$H-5 \rightarrow L+1$	$\pi(\text{hmpbta})/d \rightarrow d/\pi^*(\text{hmpbta})/\pi^*(\text{p-tol})$				
$H-5 \rightarrow L+1$	$\pi(\text{hmpbta})/d \rightarrow d/\pi^*(\text{hmpbta})/\pi^*(\text{p-tol})$	332.4	3.73	0.0333	
$H-7 \rightarrow L$	$\pi(\text{PPh}_3) \rightarrow d/\pi^*(\text{p-tol})$				
$H-2 \rightarrow L+2$	$\pi(p-tol)/\pi(hmpbta)/d \rightarrow d/\pi^*(hmpbta)/\pi^*(p-tol)$	315.2	3.93	0.0802	
$H-13 \rightarrow L$	$\pi(\text{Cl})/\pi(\text{p-tol})/\pi(\text{O}) \rightarrow d/\pi^*(\text{p-tol})$	308.6	4.02	0.0407	
$H-9 \rightarrow L+1$	$\pi(\text{PPh}_3) \rightarrow d/\pi^*(\text{hmpbta})/\pi^*(\text{p-tol})$	304.4	4.07	0.0399	
$H-1 \rightarrow L+4$	$d/\pi(hmpbta)/\pi(Cl) \rightarrow \pi^*(PPh_3)/d$	284.3	4.36	0.0304	260.2 (4.76) 24 180
$H-13 \rightarrow L+1$	$\pi(\text{Cl})/\pi(\text{p-tol})/\pi(\text{O}) \rightarrow d/\pi^*(\text{hmpbta})/\pi^*(\text{p-tol})$	280.9	4.41	0.1174	255.7 (4.85) 51 980
$H-14 \rightarrow L$	$\pi(\text{Cl})/\pi(\text{p-tol})/\pi(\text{O}) \rightarrow d/\pi^*(\text{p-tol})$	279.6	4.43	0.0349	
$H-8 \rightarrow L+2$	$\pi(\text{PPh}_3)/\pi(\text{Cl}) \rightarrow d/\pi^*(\text{hmpbta})/\pi^*(\text{p-tol})$	279.4	4.44	0.0311	
$H-14 \rightarrow L+1$	$\pi(\text{Cl})/\pi(\text{p-tol})/\pi(\text{O}) \rightarrow d/\pi^*(\text{hmpbta})/\pi^*(\text{p-tol})$	273.2	4.54	0.0302	
$H-4 \rightarrow L+3$	$\pi(\text{PPh}_3) \rightarrow d/\pi^*(\text{PPh}_3)$	254.5	4.87	0.0371	
$H-17 \rightarrow L+1$	$\pi(Cl)/\pi(hmpbta)/\pi(N) \rightarrow d/\pi^*(hmpbta)/\pi^*(p-tol)$	252.3	4.91	0.0654	
$H-6 \rightarrow L+3$	$\pi(\text{PPh}_3) \rightarrow d/\pi^*(\text{PPh}_3)$	246.6	5.03	0.0361	
$H-8 \rightarrow L+3$	$\pi(\text{PPh}_3)/\pi(\text{Cl}) \rightarrow d/\pi^*(\text{PPh}_3)$	244.0	5.08	0.0563	
$H-1 \rightarrow L+10$	$d/\pi(hmpbta)/\pi(Cl) \rightarrow \pi^*(PPh_3)/d$	239.1	5.19	0.0423	
$H-15 \rightarrow L+2$	$\pi(\text{hmpbta})/d \rightarrow d/\pi^*(\text{hmpbta})/\pi^*(\text{p-tol})$				
$H-15 \rightarrow L+2$	$\pi(\text{hmpbta})/d \rightarrow d/\pi^*(\text{hmpbta})/\pi^*(\text{p-tol})$	238.6	5.20	0.0609	
$H-1 \rightarrow L+13$	$d/\pi(hmpbta)/\pi(Cl) \rightarrow \pi^*(hmpbta)$				
$H \rightarrow L+12$	$d/\pi(hmpbta)/\pi(Cl) \rightarrow \pi^*(PPh_3)/\pi^*(hmpbta)/d$				
$H-18 \rightarrow L+1$	$\pi(Cl)/\pi(hmpbta)/\pi(N)/d \rightarrow d/\pi^*(hmpbta)/\pi^*(p-tol)$	231.6	5.35	0.0640	
$H-3 \rightarrow L+5$	$\pi(p-tol)/\pi(hmpbta)/d \rightarrow \pi^*(PPh_3)/d$	229.8	5.39	0.0305	
$H-4 \rightarrow L+5$	$\pi(\text{PPh}_3) \rightarrow \pi^*(\text{PPh}_3)/d$				
$H-19 \rightarrow L+1$	$\pi(\text{hmpbta}) \rightarrow d/\pi^*(\text{hmpbta})/\pi^*(\text{p-tol})$	228.9	5.42	0.0405	
$H-12 \rightarrow L+3$	$\pi(\text{Cl}) \rightarrow d/\pi^*(\text{PPh}_3)$	228.4	5.43	0.0347	
$H-19 \rightarrow L+1$	$\pi(\text{hmpbta}) \rightarrow d/\pi^*(\text{hmpbta})/\pi^*(\text{p-tol})$				
$H-1 \rightarrow L+13$	$d/\pi(hmpbta)/\pi(Cl) \rightarrow \pi^*(hmpbta)$	227.2	5.46	0.0434	
$H-8 \rightarrow L+4$	$\pi(\text{PPh}_3)/\pi(\text{Cl}) \rightarrow \pi^*(\text{PPh}_3)/\text{d}$	226.1	5.48	0.0313	
$H-6 \rightarrow L+5$	$\pi(\text{PPh}_3) \rightarrow \pi^*(\text{PPh}_3)/d$				

 ε – Molar absorption coefficient [dm³ mol⁻¹ cm⁻¹]; f – oscillator strength; H – highest occupied molecular orbital; L – lowest unoccupied molecular orbital.

seen as a delocalized MLLCT (*Metal–Ligand-to-Ligand CT*) transitions. The same character can be assigned to the experimental absorption at 401.3 nm.

The transitions assigned to the experimental bands at 320.0, 260.2 and 255.7 nm can be seen as mixed *Ligand–Metal Charge Transfer (LMCT), Metal–Ligand Charge Transfer (LMCT)* and *Ligand–Ligand Charge Transfer (LLCT)* transitions.

4. Conclusions

The complexes [Re(p-NC₆H₄CH₃)X₃(EPh₃)₂] (X = Cl, Br; E = As, P) have been characterized structurally and spectroscopically. Likewise as the analogous oxocomplexes [ReOX₃(EPh₃)₂] (X = Cl, Br; E = As, P), they seem to be convenient starting materials in the reactions with uninegative N,O-donor chelate ligand. [Re(p-NC₆H₄CH₃)Cl₃(PPh₃)₂] reacts with 2-(2'-hydroxy-5'-methylphenyl)benzotriazole (Hhmpbta) forming [Re(p-NC₆H₄CH₃)]. Cl₂(hmpbta)(PPh₃)]·MeCN. It is the first imido rhenium(V) compound of [Re(NAr)X₂(N–O)(PPh₃)] type with *cis*-Cl,Cl arrangement. For all the examined complexes, the structural studies and NBO analysis confirm a linear coordination mode of the p-NC₆H₄CH₃ ligand and triple bond between the rhenium and the imido ligand.

The PPh₃ molecule is *cis*-located in relation to the Re \equiv N moiety, which forces the metal nonbonding d electrons to lie in the plane perpendicular to the M \equiv N bond axis.

Supplementary data

CCDC 770324–770328 contain the supplementary crystallographic data for $C_{43}H_{37}Cl_3P_2NRe$, $C_{43}H_{37}Br_3P_2NRe$, $C_{43}H_{37}Cl_3-As_2NRe$, $C_{43}H_{37}Br_3As_2NRe$ and $C_{40}H_{35}Cl_2N_5OPRe$. These 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.

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