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

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Abstract: Novel *p*-tolylimido rhenium(V) complexes *trans*-(Cl,Cl)-[Re(*p*-NC₆H₄CH₃)Cl₂(py-2-COO)(PPh₃)]·MeCN (**1a**), *trans*-(Cl,Cl)-[Re(*p*-NC₆H₄CH₃)Cl₂(py-2-COO)(PPh₃)] (**1b**), *trans*-(Br,Br)-[Re(*p*-NC₆H₄CH₃)Br₂(py-2-COO)(PPh₃)] (**2**), *cis*-(Cl,Cl)-[Re(*p*-NC₆H₄CH₃)Cl₂(py-2-COO)(PPh₃)] (**3**), *cis*-(Br,Br)-[Re(*p*-NC₆H₄CH₃)Br₂(py-2-COO)(PPh₃)]·H₂O (**4**), *trans*-(Cl,Cl)-[Re(*p*-NC₆H₄CH₃)Cl₂(OMe)] (**5**) and *trans*-(Br,Br)-[Re(*p*-NC₆H₄CH₃)Br₂(OMe)(PPh₃)₂]·½H₂O (**6**) were synthesized. The compounds were identified by elemental analysis IR, NMR (¹H, ¹³C and ³¹P), UV-Vis spectroscopy and X-ray crystallography. Calculations at the DFT level were undertaken in order to elucidate the structural, spectroscopic and bonding properties of the *trans*-(Cl,Cl) and *cis*-(Cl,Cl) isomers of [Re(*p*-NC₆H₄CH₃)Cl₂(py-2-COO)(PPh₃)]. In the first step, extended tests of the ability of different DFT methods (B3LYP, BP86, PBE1PBE) were performed to find the best overall performer in describing the geometry of the imido Re(V) complexes; then, the electronic spectra of the *trans* and *cis* isomers of [Re(*p*-NC₆H₄CH₃)Cl₂(py-2-COO)(PPh₃)] were investigated at the TDDFT level employing PBE1PBE functional. Additional information about bonding in the compounds [Re(*p*-NC₆H₄CH₃)Cl₂(py-2-COO)(PPh₃)] were obtained by NBO analysis. The catalytic activity of the complexes incorporating picolinate ligand was studied and compared in the synthesis of *N*-substituted ethyl glycine esters from ethyl diazoacetate and amines.

Keywords: rhenium complexes, bidentate ligands, catalysts, X-ray structures, glycine derivatives

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Introduction

The widespread contemporary interest in the coordination chemistry of rhenium arises mainly from the introduction of β^- emitting isotopes ^{188}Re and ^{186}Re in radiotherapy. There is still a need for a fundamental knowledge about the structural and spectroscopic properties, redox activities, and mechanism of ligand substitution reactions to develop new and improved Re radiopharmaceuticals.¹

Another area of growing interest for rhenium(V) compounds is their application as homogeneous catalysts in different organic chemistry transformations, especially oxidation reactions.² Rhenium compounds offer some advantages with respect to other metal complexes because (a) their diverse oxidation states provide a large variety of stable complexes and (b) most rhenium complexes are insensitive to air and moisture, what makes their handling easier for synthetic purposes. After the discovery of Toste that demonstrated the ability of the high-valent oxo-rhenium complex $[\text{ReIO}_2(\text{PPh}_3)_2]$ to activate the Si–H bond of silanes and catalyze the hydrosilylation of carbonyl compounds, high-valent oxo-rhenium complexes were also investigated as catalysts for organic reductions, which represents a complete reversal from the traditional role of these compounds as oxidation catalysts.³ Espenson et al. found out that methylrhenium trioxide (CH_3ReO_3) catalyzed the reaction of primary and secondary amines with ethyl diazoacetate to give *N*-substituted glycine ethyl esters.⁴

Previously, we reported the synthesis and properties of several families of oxorhenium(V) complexes incorporating uninegative bidentate N,O-chelating ligands. The studies revealed that $[\text{ReOX}_3(\text{PPh}_3)_2]$ ($X = \text{Cl}, \text{Br}$) are excellent starting materials for the syntheses of these compounds and that the reaction course of $[\text{ReOX}_3(\text{PPh}_3)_2]$ with N,O-donor chelating ligands depends on many factors, including the type of the ligand and experimental conditions. The results also indicated that different regioisomers of resulting $[\text{ReOX}_2(\text{N}-\text{O})(\text{PPh}_3)]$ and $[\text{ReOX}(\text{N}-\text{O})_2]$ might have a significant influence on their catalyst activity.⁵

In the current paper, we have turned our attention to studies of imidorhenium(V) complexes and we examined the reactivity of pyridine-2-carboxylic acid (py-2-COOH) towards $[\text{Re}(p\text{-NC}_6\text{H}_4\text{CH}_3)\text{X}_3(\text{PPh}_3)_2]$ ($X = \text{Cl}, \text{Br}$). The complexes $[\text{Re}(p\text{-NC}_6\text{H}_4\text{CH}_3)\text{X}_3(\text{PPh}_3)_2]$ can be considered as analogues of $[\text{ReOX}_3(\text{PPh}_3)_2]$. The imido core NR^{2-} is isoelectronic to O^{2-} and compounds $[\text{Re}(p\text{-NC}_6\text{H}_4\text{CH}_3)\text{X}_3(\text{PPh}_3)_2]$ and $[\text{ReOX}_3(\text{PPh}_3)_2]$ showed similar ligation around Re(V) atom with halide ligands arranged in *meridional* fashion and triphenylphosphine molecules *trans* located to each other.⁶

Herein, several novel imidorhenium(V) complexes, *trans*-(Cl,Cl)- $[\text{Re}(p\text{-NC}_6\text{H}_4\text{CH}_3)\text{Cl}_2(\text{py-2-COO})(\text{PPh}_3)] \cdot \text{MeCN}$ (**1a**), *trans*-(Cl,Cl)- $[\text{Re}(p\text{-NC}_6\text{H}_4\text{CH}_3)\text{Cl}_2(\text{py-2-}$

COO)(PPh₃)] (**1b**), *trans*-(Br,Br)-[Re(*p*-NC₆H₄CH₃)Br₂(py-2-COO)(PPh₃)] (**2**), *cis*-(Cl,Cl)-[Re(*p*-NC₆H₄CH₃)Cl₂(py-2-COO)(PPh₃)] (**3**), *cis*-(Br,Br)-[Re(*p*-NC₆H₄CH₃)Br₂(py-2-COO)(PPh₃)]·H₂O (**4**), *trans*-(Cl,Cl)-[Re(*p*-NC₆H₄CH₃)Cl₂(OMe)(PPh₃)₂] (**5**) and *trans*-(Br,Br)-[Re(*p*-NC₆H₄CH₃)Br₂(OMe)(PPh₃)₂]·½H₂O (**6**), are reported and characterized structurally and spectroscopically. Calculations at the DFT level were undertaken to elucidate the structural, spectroscopic and bonding properties of the *trans*-(Cl,Cl) and *cis*-(Cl,Cl) isomers of [Re(*p*-NC₆H₄CH₃)X₂(py-2-COO)(PPh₃)]. The catalytic activity of the complexes incorporating picolinate ligand was studied and compared in the synthesis of *N*-substituted ethyl glycine esters from ethyl diazoacetate and amines.

Results and Discussion

Synthesis of the complexes. The complexes *trans*-(Cl,Cl)-[Re(*p*-NC₆H₄CH₃)Cl₂(py-2-COO)(PPh₃)]·MeCN (**1a**), *trans*-(Cl,Cl)-[Re(*p*-NC₆H₄CH₃)Cl₂(py-2-COO)(PPh₃)] (**1b**), *trans*-(Br,Br)-[Re(*p*-NC₆H₄CH₃)Br₂(py-2-COO)(PPh₃)] (**2**), *cis*-(Cl,Cl)-[Re(*p*-NC₆H₄CH₃)Cl₂(py-2-COO)(PPh₃)] (**3**) and *cis*-(Br,Br)-[Re(*p*-NC₆H₄CH₃)Br₂(py-2-COO)(PPh₃)]·H₂O (**4**) were prepared by metathesis reactions between [Re(*p*-NC₆H₄CH₃)X₃(PPh₃)₂] and the carboxylic ligand. Interestingly, the reactions of [Re(*p*-NC₆H₄CH₃)X₃(PPh₃)₂] with py-2-COOH were independent of the molar ratio of the ligand to metal precursor. Only complexes with one chelating ligand were obtained even when excess of picolinic acid was used. On the other hand, the reactions were found to be solvent dependent. They resulted in the formation of *trans*-(Cl,Cl)-[Re(*p*-NC₆H₄CH₃)Cl₂(py-2-COO)(PPh₃)]·MeCN (**1a**) and *trans*-(Br,Br)-[Re(*p*-NC₆H₄CH₃)Br₂(py-2-COO)(PPh₃)] (**2**) when the reactions were carried out in acetonitrile. However, refluxing of [Re(*p*-NC₆H₄CH₃)X₃(PPh₃)₂] with py-2-COOH in methanol led to a mixture of the compounds *trans*-(Cl,Cl)-[Re(*p*-NC₆H₄CH₃)Cl₂(py-2-COO)(PPh₃)] (**1b**) and *cis*-(Cl,Cl)-[Re(*p*-NC₆H₄CH₃)Cl₂(py-2-COO)(PPh₃)] (**3**) for [Re(*p*-NC₆H₄CH₃)Cl₃(PPh₃)₂], and *trans*-(Br,Br)-[Re(*p*-NC₆H₄CH₃)Br₂(py-2-COO)(PPh₃)] (**2**) and *cis*-(Br,Br)-[Re(*p*-NC₆H₄CH₃)Br₂(py-2-COO)(PPh₃)]·H₂O (**4**) for [Re(*p*-NC₆H₄CH₃)Br₃(PPh₃)₂]. We anticipated that compounds [Re(*p*-NC₆H₄CH₃)X₃(PPh₃)₂] might react with methanol, exhibiting a different reactivity pattern from that in acetonitrile. As expected, the reactions of [Re(*p*-NC₆H₄CH₃)X₃(PPh₃)₂] with methanol afforded methoxy imido complexes *trans*-(Cl,Cl)-[Re(*p*-NC₆H₄CH₃)Cl₂(OMe)(PPh₃)₂] (**5**) and *trans*-(Br,Br)-[Re(*p*-NC₆H₄CH₃)Br₂(OMe)(PPh₃)₂]·½H₂O (**6**) as a result of the replacement of the labile X ligand *trans* to imido group with the methoxy ion coming from methanol. This behaviour is related

to that observed for oxocomplexes $[\text{ReOX}_3(\text{PPh}_3)_2]$ in which the X ligand *trans* to the oxo group is readily exchanged by the methoxy group giving $[\text{ReOX}_2(\text{OMe})(\text{PPh}_3)_2]$.⁷ The complexes **5** and **6**, treated with py-2-COOH, gave compounds **3** and **4** with the halide ligands in *cis* relative dispositions (Scheme 1).

Scheme 1. Formation of complexes **1-6**.

All complexes **1-6** show high stability toward air and moisture both in the solid state and in solution for several weeks at ambient temperature. Configurational stability of *cis* and *trans* isomers of $[\text{Re}(p\text{-NC}_6\text{H}_4\text{CH}_3)\text{X}_2(\text{py-2-COO})(\text{PPh}_3)]$ in solution at room temperature was confirmed by NMR spectroscopy. No *cis-trans* isomerism in solution was evidenced by NMR studies.

Since the imido core NR^{2-} is isoelectronic to O^{2-} and tends to form analogous complexes with rhenium, a short comparison with Re(V) oxocompounds is worthy. The majority of the reported oxorhenium(V) complexes $[\text{ReOX}_2(\text{N-O})(\text{PPh}_3)]$ of uninegative bidentate N,O-chelating ligand have *cis*-arranged halide ions.⁸ A rare *trans*-X,X conformation has been found in $[\text{ReCl}_2(\text{APO})(\text{PPh}_3)]$, $[\text{ReOCl}_2(\text{DPO})(\text{PPh}_3)]$,⁹ $[\text{ReOX}_2(\text{hbt})(\text{PPh}_3)]$ ^{4a} and

[ReOX₂(hpb)(PPh₃)]^{4b} (APOH = 4-anilino-3-penten-2-one; DPOH = 4-[2,6-dimethylanilino]-3-penten-2-one, Hhbt = 2-(2'-hydroxyphenyl)-2-benzothiazole and Hhpb = 2-(2'-hydroxyphenyl)-1*H*-benzimidazole. As far as [ReOX₂(py-2-COO)(PPh₃)] is concerned, only the *cis*-(X,X) isomers have been synthesized and characterized so far.¹⁰

For compounds [Re(NAr)X₂(N-O)(PPh₃)], the *trans*-X,X arrangement of halide ions seems to be favoured, although the imido rhenium complexes incorporating uninegative N,O-donor chelate ligands are distinctly less elaborated.¹¹ Calculations at the DFT level were undertaken for *trans*-(Cl,Cl)- and *cis*-(Cl,Cl)-[Re(*p*-NC₆H₄CH₃)Cl₂(py-2-COO)(PPh₃)] to get a deeper insight into the structural, spectroscopic and bonding properties of isomeric forms.

IR and ¹H NMR spectra. The IR spectra of **1a**, **1b**, **2**, **3** and **4** are dominated by very strong bands (at 1679 cm⁻¹ for **1a**, 1679 cm⁻¹ for **1b**, 1677 cm⁻¹ for **2**, 1690 cm⁻¹ for **3** and 1682 cm⁻¹ for **4**) assigned to ν_{as}(CO₂) stretching mode. Strong ν_s(CO₂) bands are found at 1313 and 1282 cm⁻¹ for **1a**·MeCN, 1314 and 1282 cm⁻¹ for **1b**, 1312 and 1287 cm⁻¹ for **2**, 1314 and 1278 cm⁻¹ for **3** and 1314 and 1280 cm⁻¹ for **4**. High values of Δν(CO₂)=ν_{as}(CO₂)-ν_s(CO₂) (equal to ≈350 cm⁻¹) reflect a unidentate coordination mode of carboxylate group in the [Re(*p*-NC₆H₄CH₃)X₂(py-2-COO)(PPh₃)] compounds.¹² For *trans*-(X,X) and *cis*-(X,X) isomers of [Re(*p*-NC₆H₄CH₃)X₂(py-2-COO)(PPh₃)], these absorptions are very similar and they are no distinctive for molecular structure determination. This conclusion was confirmed by calculations. The calculated ν_{as}(CO₂) and ν_s(CO₂) are almost identical for both *trans*-(X,X) and *cis*-(X,X), despite the different molecular symmetry of these isomers (1820, 1370 and 1333 cm⁻¹ for **1** and 1814, 1363 and 1336 cm⁻¹ for **3**). In comparison with the experimental data, however, these values are shifted to higher frequencies by ~8%, which is an usual feature for this approach (*Figure S1*).

The calculated ν(Re–NC₆H₄CH₃) frequencies appear at 1555, 1447 and 1063 cm⁻¹ for **1**, and 1555, 1453 and 1065 cm⁻¹ for **3**. Experimentally these vibrations are difficult to identify as the ν(Re–NC₆H₄CH₃) stretches are mixed with ν_{C=N} and ν_{P–C} modes of PPh₃ and py-2-COO⁻ ligands.¹¹

¹H NMR spectra made possible to distinguish between *cis* and *trans* stereoisomers of [Re(*p*-NC₆H₄CH₃)X₂(py-2-COO)(PPh₃)] (*Figure S2*). Distinctive signals attributed to the methyl protons of the *p*-tolylimido group of **1a**, **1b**, **2**, **3** and **4** appear in the range 2.30–2.20 ppm. The aromatic region is dominated by signals of triphenylphosphine protons, which obscure some protons of the arylimido group. For both isomers, the signals of picolinate

ligand are shifted upfield in comparison with the free ligand (doublet at 8.70 and multiplet at 8.08–7.94) due to coordination to rhenium atom. The stronger upfield shift of these signals in *cis*-(X,X) isomers is consistent with an electron transfer occurring from the halide ion into the *trans* pyridine ring of picolinate ligand.

The coordination of the phosphine in $[\text{Re}(p\text{-NC}_6\text{H}_4\text{CH}_3)\text{X}_2(\text{py-2-COO})(\text{PPh}_3)]$ and $[\text{Re}(p\text{-NC}_6\text{H}_4\text{CH}_3)\text{X}_2(\text{OMe})(\text{PPh}_3)_2]$ was additionally confirmed by ^{31}P NMR spectroscopy. As expected, the single phosphorus signals, observed for **1-6** in the range 25.57–25.65 ppm, are downfield from uncoordinated triphenylphosphine (–6 ppm).

Molecular Structures. A definite proof for the structures of **1-6** was provided by the X-ray diffraction results (Tables 1 and S1; Figures 1 and 2).

(Table 1, Figures 1 and 2)

The complexes **1a**, **1b**, **2**, **3** and **4** show octahedral geometry about the central rhenium atom defined by the *p*-methylphenylimido group, two halide ions, the phosphorus atom of PPh_3 molecule, and the carboxylate chelate ligand. X-Ray studies revealed two different ligand arrangements in these compounds. The halide ions of **1a**, **1b** and **2** are in *trans* relative dispositions, whereas the complexes **3** and **4** were found to be *cis*-(X,X) isomers. In all these compounds the oxygen atom of carboxylate ligand occupies *trans* position to the *p*-methylphenylimido ion. This occupancy is justified by *trans*-influence of imido group forcing harder oxygen atom of the N–O ligand into the *trans* position. Triphenylphosphine molecule with its π -acidity adopts *cis* disposition with respect to the linear $\text{RN}\equiv\text{Re}-\text{O}$ core and stabilizes it due to accessible π -donation from rhenium to PPh_3 molecule. Interestingly, no extraordinary differences in terms of bond lengths and angles can be noticed between *cis*-(X,X) and *trans*-(X,X) isomers of $[\text{Re}(p\text{-NC}_6\text{H}_4\text{CH}_3)\text{X}_2(\text{py-2-COO})(\text{PPh}_3)]$. The $\text{Re}-\text{N}_{\text{imido}}-\text{C}_{\text{imido}}$ bond angles of $167.9(6)^\circ$ in **1a**, $171.9(10)^\circ$ in **1b**, $173.1(10)^\circ$ in **2**, $174.4(3)^\circ$ in **3** and $175.1(3)^\circ$ in **4** agree with a linear coordination mode of the arylimido ligands ($167\text{--}176^\circ$), and these values are 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 exist. The $\text{Re}-\text{N}_{\text{imido}}$ bond lengths of $1.708(6)$ Å in **1a**, $1.650(17)$ Å in **1b**, $1.708(11)$ Å in **2**, $1.708(4)$ Å in **3** and $1.717(3)$ Å in **4** fall in the range typical of mononuclear complexes of rhenium(V) having $[\text{Re}\equiv\text{NR}]^{3+}$ core, and reflect the expected triple $\text{Re}\equiv\text{N}$ bond.^{6,11} The interatomic distance between the rhenium atom and carboxylate oxygen atom is

almost equal to an ideal single Re–O bond length (*ca.* 2.04 Å),¹³ indicating lack of delocalization in the RN≡Re–O unit.

The complexes **5** and **6** were found to be *trans*-(X,X) isomers with methoxy ligand *trans* to the Re≡NR moiety. The elongation of the Re–N_{imido} (in comparison with the corresponding values for **1–4**) is accompanied by shortening of Re–O distance *trans* to the Re≡NR moiety. It is a consequence of the competition of the methoxy ion with imido group in the interaction with the dπ orbitals of the metal. The Re–OCH₃ distances in **5** [1.915(3) Å] and **6** [1.898(3) Å] indicate a significant double-bond character.¹⁴ The larger delocalization of electron density in the linear RN≡Re–OCH₃ core results in less pronounced electron transfer by π donation to the equatorial P atoms. In compounds **5** and **6**, phosphorus atoms form considerably longer Re–P bond lengths as compared to complexes **1–4**.

DFT calculations. In the first step, extended tests of the ability of different DFT methods (B3LYP, BP86, PBE1PBE) to find the best overall performer in describing geometry of the imido Re(V) complexes were performed. The geometries of *trans*-(Cl,Cl)-[Re(*p*-NC₆H₄CH₃)Cl₂(py-2-COO)(PPh₃)] and *cis*-(Cl,Cl)-[Re(*p*-NC₆H₄CH₃)Cl₂(py-2-COO)(PPh₃)] were optimized in singlet states using three DFT methods (B3LYP, BP86, PBE1PBE) in combination with several basis sets given in Table 2.

(Table 2)

All the methods give acceptable deviations between the experimental and theoretical geometric data. The largest deviations were found for BP86 procedure, whereas both geometries were best reproduced by employing the PBE1PBE method (Table S2). It gives an excellent estimation of Re–N_{imido} bond lengths with deviations smaller than 0.003 Å. Deviations of the distance Re–N_{imido} for the methods B3LYP, BP86 are larger, from 0.009 to 0.014 Å for B3LYP, and from 0.030 to 0.033 Å for BP86 (Figure S3). The Re–N_{py} and Re–O bond lengths are also well reproduced with errors ranging from –0.004 to –0.035 Å for Re–N_{py} and from –0.017 to –0.037 Å for Re–O. Larger deviations, especially for B3LYP functional, were noticed for Re–Cl bond lengths, but they are also satisfactory for this level of theory. The Re–Cl elongation is consistent with the research of Turki et al. The authors addressed that the drawback of DFT arises from the dynamical correlation effects, which become very important in complexes with a polar M–Cl bond.¹⁵ This issue can be partly solved by using dispersion corrected functional in DFT method, as indicated by the results for

dispersion corrected B3LYP functional (*Table S2*). Further calculations were performed using PBE1PBE method in combination with the basis sets appointed in *Table 2* as LTZ631+. View Article Online
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For both compounds, the calculated charge on the rhenium atom is considerable lower than the formal charge +5 as a product of significant charge donation from ligands to d_{Re} orbitals in the examined structures (*Table 3*). Less positive charge on the rhenium atom in *cis*-(Cl,Cl) isomer can be correlated with higher electron density delocalization from Cl ligands towards the rhenium center occurring for this ligand arrangement. The Cl ligands of *trans*-(Cl,Cl) isomer are more negatively charged as compared to *cis*-(Cl,Cl) one. For the other donor atoms of coordination sphere no significant variations in the calculated atomic charges are observed between **1** and **3**.

(*Table 3*)

For further understanding of the bond characteristics in reported isomers of $[\text{Re}(p\text{-NC}_6\text{H}_4\text{CH}_3)\text{Cl}_2(\text{py-2-COO})(\text{PPh}_3)]$, natural bond orbital (NBO) studies have been performed. For *cis*-(Cl,Cl)- $[\text{Re}(p\text{-NC}_6\text{H}_4\text{CH}_3)\text{Cl}_2(\text{py-2-COO})(\text{PPh}_3)]$ complex, the results of NBO point to the existence of one σ and two π natural $\text{Re-N}_{\text{imido}}$ orbitals. Both σ and π bonds are strongly polarized towards the nitrogen atom. The hybridization at rhenium shows clearly that d contribution dominates the metal bonding in σ and π $\text{Re-N}_{\text{imido}}$ bonds. For π bonds the nitrogen atom of the imido ligand employs pure or quasi pure p atomic orbitals (*Figure S4b*).

For *trans*-(Cl,Cl) isomer, two $\text{Re-N}_{\text{imido}}$ natural bond orbitals were confirmed by NBO analysis. Both orbitals result from 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, and they are of π character (*Figure S4a*). Lack of $\sigma_{\text{Re-NR}}$ natural orbital indicates a conceivable predominant Coulomb-type Re-ligand interaction¹⁶. The nature of $\text{Re-N}_{\text{imido}}$ bonds is in agreement with the results obtained in previous works regarding analysis of the bonding nature of rhenium imido complexes.^{5,11}

The triple bond character of $\text{Re-N}_{\text{imido}}$ in **1** and **3** is also indicated by the Wiberg bond indices (*Table 4*). For both complexes **1** and **3**, the Wiberg bond indices of $\text{Re}(1)\text{-N}(2)$ are over three times larger than those of $\text{Re}(1)\text{-N}(1)$ in **1** and $\text{Re}(1)\text{-N}(1)$ in **3**.

(*Table 4*)

All used functionals and basis sets led to the higher stability of the *cis*-isomer, but the energy difference between *trans*-(Cl,Cl) and *cis*-(Cl,Cl) isomers is remarkably small (1.92-3.74 kcal/mol), indicating that their formation is kinetically rather than thermodynamically controlled.

Schematic representation of the energy levels with the partial frontier molecular orbital compositions of **1** and **3** is presented in Figure 3. The contours of the selected frontier orbitals are depicted in Figure 4. As can be seen from Figures 3 and 4, only small variations on the frontier molecular orbital energies and orbital compositions were observed with regard to the relative position of halide ions in $[\text{Re}(p\text{-NC}_6\text{H}_4\text{CH}_3)\text{Cl}_2(\text{py-2-COO})(\text{PPh}_3)]$. The HOMO of these complexes presents significant metallic character and it is mainly constituted by rhenium d_{xy} orbital (62% for **1** and 65% for **3**) in antibonding relation to chloride occupied p orbitals (30% for **1** and 25% for **3**). For *cis*-(Cl,Cl) isomer, this molecular orbital is also insignificantly contributed by picolinate ligand (10%).

The HOMO-1 orbital is 1.16 eV for **1** and 0.96 eV for **3** lower in energy in relation to the highest occupied molecular orbital and presents a high contribution of the *p*-methylphenylimido ligand (70% for **1** and 72% for **3**). The contribution of this ligand is due to the interaction of a bonding p orbital with a metallic d_π orbital (14% for **1** and 13% for **3**). To a large extent, the HOMO-1 of **1** and **3** can be considered as $\pi_{\text{Re}\equiv\text{NR}}$ orbital. For *cis*-(Cl,Cl) isomer, also a moderated contribution from the antibonding interaction of rhenium d_π orbital with Cl orbitals (12%) is observed in this molecular orbital. In turn, the HOMO-1 of **1** is contributed by triphenylphosphine orbitals (10%). The other high-lying occupied orbitals are mainly centered on the triphenylphosphine orbitals.

The LUMO of these complexes presents a high contribution of the *p*-methylphenylimido ligand, mainly from the interaction between the π^* -antibonding orbital and d_π rhenium orbital. A significant contribution of $\pi^*_{\text{Re}\equiv\text{NR}}$ orbitals is also observed in LUMO+1 and LUMO+2 of **1** and **3**. Unlike to LUMO, however, these MOs are predominantly localized on the π^* -antibonding orbitals of picolinate ligand.

By comparing the FMO energy levels of **1** and **3**, it can be found an insignificant increase in the energy gap HOMO–LUMO for *cis*-(Cl, Cl) isomer (3.28 for **1** and 3.46 eV **3**). For this geometry, the energy level of HOMO level is stabilized whereas the energy level of LUMO is slightly raised compared with complex **1**.

(Figures 3 and 4)

Electronic spectra. The complexes **1** and **3** have similar absorption character and TDDFT transitions well correlate with the experimental absorptions, as illustrated in Figure 5.

(Figure 5)

The low-energy absorption bands observed at 791.2 and 602.4 for **1** and 763.6 and 617.6 nm for **3** are contributed by transitions HOMO→LUMO and HOMO→LUMO+1 either for *cis*-(Cl,Cl) or *trans*-(Cl,Cl) isomer (Tables S3 and S4). Analysis of the corresponding orbitals clearly shows that these transitions can be described as mixed d→d (*Ligand Field*; *LF*), $d\pi(\text{Cl}) \rightarrow d_{\text{Re}}$ (*Ligand-Metal Charge Transfer*; *LMCT*) and $\pi(\text{Cl}) \rightarrow \pi^*(p\text{-tol})/\pi^*(\text{py-2-COO})$ (*Ligand-Ligand Charge Transfer*; *LLCT*) transitions or a delocalized *MLLCT* (metal–ligand-to-ligand CT) description also can be used. The blue shift of the lowest-energy absorption band for **3** well correlates with increase of HOMO-LUMO for this complex.

The experimental absorptions at 425.6 nm for *trans*-(Cl,Cl) isomer and 418.0 for *cis*-(Cl,Cl), assigned to HOMO→LUMO+2 transition, can be seen as mixed d→d, $\pi(\text{Cl}) \rightarrow d_{\text{Re}}$, $d_{\text{Re}} \rightarrow \pi^*(\text{py-2-COO})/\pi^*(p\text{-tol})$ and $\pi(\text{Cl}) \rightarrow \pi^*(\text{py-2-COO})/\pi^*(p\text{-tol})$ transitions. The intense bands in high energy region are largely attributed to *Ligand-Ligand Charge Transfer* and interligand (*IL*) transitions.

Catalytic activity. The catalytic activity of the complexes reported herein was tested in the reaction of amines with ethyl diazoacetate leading to *N*-substituted glycine ethyl esters.⁴ Aniline (**7a**) was selected as the model substrate in order to better assess the selectivity of the catalysts due to the presence of two N–H bonds that could lead to products **9a** and **10a** (Scheme 2 and Table 5).

Scheme 2. The reaction of aniline with ethyl diazoacetate catalyzed by the rhenium complexes.

(Table 5)

Initial studies with the complex *trans*-Cl,Cl (**1**) at 70 °C under air, either in toluene or without solvent gave poor conversions (Table 5, entries 1 and 2). A promising 42% conversion into product **9a** was, however, noted when the reaction was carried out under an argon atmosphere (Table 5, entry 3). This result could be somewhat improved when using *trans*-Br,Br (**2**) as catalyst, albeit a substantial amount of product **10a** was obtained (Table 5, entry 4). Interestingly, the formation of the latter could be prevented when double amount of the catalyst was utilized (Table 5, entry 5), whereas microwave irradiation did not have any influence in the reaction rate (Table 5, entry 6). Higher conversion was achieved for **9a** with

cis-Cl₂ (3) under solvent-free conditions, which was formed together with minor amounts of **10a** (Table 5, entry 7). Reactions with *cis*-Cl₂ (3) conducted either at room temperature or in manifold organic solvents proved to be inefficient (Table 5, entries 8–16). Slightly higher conversion was recorded using double amount of *cis*-Cl₂ (3), with concomitant formation of **10a** (Table 5, compare entries 7 and 17). Under the latter conditions, the presence of air was shown to have a deleterious effect on the performance of the catalyst (Table 5, entry 18), as also observed for *trans*-Cl₂ (1) (Table 5, entries 1 and 2). Finally, *cis*-Br₂ (4) behaved similar to *trans*-Br₂ (2) (Table 5, compare entries 4 and 19), with the stereochemistry of the complexes having no apparent effect in the yield.

Better results were attained when the secondary amines *N*-methylaniline (**7b**) and piperidine (**7c**) were subjected to the conditions in entry 17 (Table 5). A single product was detected in both cases, with the piperidine derivative being obtained in almost quantitative yield (Scheme 3). It is noteworthy that, under the aforementioned conditions, complex *cis*-Cl₂[Re] (3) was shown to be superior in the latter reaction (**9c**, 95% yield) when compared with the other complexes studied, namely, *trans*-Cl₂[Re] (1) (**9c**, 31% yield), *trans*-Br₂[Re] (2) (**9c**, 53% yield), and *cis*-Br₂[Re] (4) (**9c**, 19% yield).

Scheme 3. Solvent-free reaction of secondary amines and ethyl diazoacetate catalyzed by the rhenium complex *cis*-Cl₂Cl (3).

The transition-metal catalyzed N-H insertion reaction of diazocarbonyl compounds is generally considered a stepwise process in which the role of the metal is not yet well understood.¹⁷ In the reaction of ethyl diazoacetate with primary amines catalyzed by methylrhenium trioxide, Espenson et al. proposed the formation of a three-membered metallaoxacycle methylrhenium dioxide (derived from ethyl diazoacetate), which undergoes

nucleophilic attack by the amine at the carbon atom of the metallacycle.⁴ In our case, the scenario is rather different as no Re=O bonds are present in the complexes. Therefore, we propose the nucleophilic attack of the amine occurring on the electrophilic Re carbene **10** to form an ammonium ylide (**11**), which undergoes a 1,2-rearrangement to transfer a proton from nitrogen to carbon with regeneration of the catalyst (Scheme 4).

The fact that methylrhenium trioxide attained higher yields than our complexes, in the reaction of primary amines with ethyl diazoacetate, could be due to the higher electrophilic character of the carbon-reacting center in the corresponding intermediate, given that Re(VII) species are involved instead of the Re(V) of our complexes. Indeed, the calculated charge on the rhenium atom in **1** and **3** was found to be considerable lower than the formal charge +5 (see above). However, in the case of the reaction of ethyl diazoacetate with secondary amines (Scheme 3), the fact that there is only one reactive N-H bond together with their higher nucleophilicity could account for the better yields observed.

Scheme 4. Proposed reaction mechanism.

A comparison between the reactivity of the complexes **1–4** seems more difficult to establish. On one hand, the less positive charge on the rhenium atom in *cis*-(Cl,Cl) isomer, when compared with that in *trans*-(Cl,Cl), points to a favoured nucleophilic attack in the derived carbene of the latter (more electrophilic). However, the product conversion was higher for *cis*-(Cl,Cl) (67% vs. 42%). At any rate, we must take into account that the Re

atomic charges from the Natural Population Analysis (NPA) (Table 4) are small and probably, not different enough to allow the explanation of the differences found in reactivity. On the other hand, the NBO studies revealed the existence of one σ and two π bonds of Re–N_{imido} in *cis*-(Cl,Cl), strongly polarized towards the nitrogen atom, and the lack of $\sigma_{\text{Re-NR}}$ natural orbital in *trans*-(Cl,Cl), what might indicate a lower stability of the latter complex affecting its reactivity.

As regards the reactivity of the dibromo complexes **2** and **4** with ethyl diazoacetate and aniline, the conversion was the same in both cases (54%) and somewhat lower than with *cis*-(Cl,Cl) (**1**). Therefore, the stereochemistry seems not to play an important role in this particular reaction. The differences in reactivity were more pronounced in the reaction of ethyl diazoacetate and piperidine, a more nucleophilic and bulkier amine than aniline (Scheme 3). In this case, the higher electrophilicity conferred to the complex by the two Cl ligands (more electronegative than Br), together with the lower steric hindrance imparted by Cl to the complex when compared with Br, could explain the higher conversion recorded for the *cis*-(Cl,Cl), the stereochemistry being important in this case.

Another aspect that could be considered is the ligand exchange in the formation of the Re carbene **10**. If we suppose that PPh₃ is the ligand exchanged by the carbene derived from ethyl diazoacetate (we always detect some PPh₃ as by-product),¹⁸ this exchange could be more favoured for a certain stereochemistry on the basis of steric factors or the strength of the interaction of PPh₃ with the metal. On this basis, PPh₃ might interact stronger with the more positively charged Re in *trans*-(Cl,Cl), making the ligand exchange more difficult and resulting in lower yield than with *cis*-(Cl,Cl).

Although the methodology of Espenson's group, involving MeReO₃, produced compound **9a** in a higher yield (89%) under milder reaction conditions, the long reaction times applied and the use of dry benzene as solvent curtail its practical application.⁴ In contrast, the procedure presented herein is more environmentally benign, with the reactions proceeding in moderate-to-excellent yields under solvent-free conditions.

Conclusions

The reactivity of [Re(*p*-NC₆H₄CH₃)Cl₃(PPh₃)₂] (X = Cl, Br) towards pyridine-2-carboxylic acid has been examined and compared with the related exchange reactions performed with oxocompounds [ReOX₃(PPh₃)₂]. As a result of these studies, six novel rhenium(V) imidocomplexes have been obtained and characterized structurally and spectroscopically. In the isomers *trans*-(X,X)-[Re(*p*-NC₆H₄CH₃)X₂(py-2-COO)(PPh₃)] and *cis*-(X,X)-[Re(*p*-

$\text{NC}_6\text{H}_4\text{CH}_3)_2\text{X}_2(\text{py-2-COO})(\text{PPh}_3)]$, pyridine-2-carboxylate ion is coordinated in a chelate way via N- and O-donor atoms, and the PPh_3 molecule is *cis*-located in relation to the $\text{Re}\equiv\text{N}$ moiety, which forces the metal nonbonding *d* electrons to lie in the plane perpendicular to the $\text{M}\equiv\text{N}$ bond axis. The X-ray studies and NBO analysis confirm a linear coordination mode of the *p*- $\text{NC}_6\text{H}_4\text{CH}_3$ ligand and triple bond between the rhenium and the imido ligand. The caboxylate imido rhenium complexes have been shown to be catalytically active in the reaction of aniline and ethyl diazoacetate under solvent-free conditions. The complex *cis*-(Cl,Cl)- $[\text{Re}(p\text{-NC}_6\text{H}_4\text{CH}_3)\text{Cl}_2(\text{py-2-COO})(\text{PPh}_3)]$ (**3**) has reached a maximum 67% conversion into *N*-phenyl ethyl glycine ester, with the product of double carbene insertion being normally obtained as a side-product. In contrast, secondary amines have led to single *N*-substituted ethyl glycine esters in moderate-to-excellent yields.

Experimental Section

Materials

All chemicals and bidentate ligands were purchased from commercial sources and were used without further purification. The complexes *mer*- $[\text{Re}(p\text{-NC}_6\text{H}_4\text{CH}_3)\text{X}_3(\text{PPh}_3)_2]$ ($\text{X} = \text{Cl}, \text{Br}$) were prepared according to the literature methods.¹⁹

Instrumentation

IR spectra were recorded on a Nicolet Magna 560 spectrophotometer in the spectral range 4000-400 cm^{-1} with the samples in form of KBr pellets. The ^1H 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 ^1H NMR spectra, 125 MHz for ^{13}C NMR spectra and 162 MHz for ^{31}P NMR using DMSO-d_6 as solvent and TMS as an internal standard. The X-ray intensity data of **1-6** were collected on a Gemini A Ultra diffractometer equipped with Atlas CCD detector and graphite monochromated MoK_α radiation ($\lambda = 0.71073\text{\AA}$) 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.²⁰ 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. SHELXS97 and SHELXL97 programs were used for all the calculations.²¹ Atomic scattering factors were those incorporated in the computer programs.

CCDC- 899354 (for **1a**), - 936243 (for **1b**), - 899355 (for **2**), - 899356 (for **3**), - 899357 (for **4**), - 936244 (for **5**) and - 936245 (for **6**) 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.

Preparation of complexes **1a** and **2**

mer-[Re(*p*-NC₆H₄CH₃)Cl₃(PPh₃)₂] (0.43g, 0.54 mmol) or [Re(*p*-NC₆H₄CH₃)Br₃(PPh₃)₂] (0.52g, 0.54 mmol) was added to pyridine-2-carboxylic acid (0.07 g, 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 green crystalline precipitate of *trans*-(Cl,Cl)-[Re(*p*-NC₆H₄CH₃)Cl₂(py-2-COO)(PPh₃)]·MeCN (**1a**) or *trans*-(Br,Br)-[Re(*p*-NC₆H₄CH₃)Br₂(py-2-COO)(PPh₃)] (**2**) was filtered off and dried in the air. X-ray quality green crystals of **1**·MeCN and **2** were obtained by slow recrystallization from acetonitrile, and collected in 80 and 75% yield, respectively.

***trans*-(Cl,Cl)-[Re(*p*-NC₆H₄CH₃)Cl₂(py-2-COO)(PPh₃)]·MeCN (**1a**):** IR (KBr; ν/cm^{-1}): 3063(w), 1679(vs), 1605(w), 1590(s), 1482(m), 1462(w), 1434(s), 1361(m), 1313(s), 1282(s), 1252(m), 1172(w), 1141(m), 1094(s), 1055(w), 1018(w), 853(m), 824(m), 767(w), 746(s), 705(sh), 693(s), 574(w), 527(s), 510(m), 493(sh), and 456(w).

C₃₃H₂₉Cl₂N₃O₂Pre (787.66): calcd. C 50.32, H 3.71, N 5.33; found C 50.59, H 3.62, N 5.24%.

¹H NMR (DMSO, ppm): δ = 8.18(d, 1H, 7.8Hz), 8.07(td, 1H, 7.7Hz, 1.4Hz), 7.98(d, 1H, 5.5Hz), 7.91(ddd, 1H, 8.0Hz, 4.7Hz, 1.9Hz), 7.61(ddd, 6H, 11.3Hz, 7.9Hz, 1.5Hz), 7.51 – 7.40(m, 11H), 7.25(d, 2H, 8.1Hz), 2.27(s, 3H) and 2.09 (s, 3H).

¹³C NMR (125 MHz, DMSO-d₆): δ = 154.2, 148.2, 147.0, 143.0, 141.9, 134.6, 134.5, 131.8, 131.7, 131.5, 131.3, 129.8, 128.9, 128.8, 126.4, 121.9, 118.5, 22.4, 1.62 ppm.

³¹P NMR (DMSO-d₆): δ = 25.58 ppm.

***trans*-(Br,Br)-[Re(*p*-NC₆H₄CH₃)Br₂(py-2-COO)(PPh₃)] (**2**):** IR (KBr; ν/cm^{-1}): 3051(w), 1677(vs), 1614(m), 1588(s), 1481(m), 1448(w), 1435(s), 1357(m), 1312(s), 1287(s), 1248(m),

1173(w), 1153 (m), 1092(s), 1055(w), 1017(w), 855(m), 822(m), 747(s), 705(sh), 694(s), 563(w), 528(s), 598(m), 497(m) and 457(w).

C₃₁H₂₆Br₂N₂O₂Pre (835.53): calcd. C 44.56, H 3.14, N 3.35; found C 44.83, H 3.19, N 3.38%.

¹H NMR (DMSO, ppm): δ = 8.18(d, 1H, 7.8Hz), 8.09 – 8.05(m, 1H), 8.02(d, 1H, 5.4Hz), 7.96 – 7.92(m, 1H), 7.68 – 7.59(m, 6H), 7.53 – 7.45(m, 11H), 7.26(d, 2H, 8.2Hz) and 2.28(s, 3H).

¹³C NMR (125 MHz, DMSO-d₆): δ = 154.3, 148.6, 147.0, 142.8, 142.3, 134.7, 134.6, 131.6, 128.8, 128.2, 121.7, 22.4 ppm.

³¹P NMR (DMSO-d₆): δ = 25.65 ppm.

Preparation of complexes **1b** and **3**

[Re(*p*-NC₆H₄CH₃)Cl₃(PPh₃)₂] (0.48 g, 0.54 mmol) was added to pyridine-2-carboxylic acid (0.07 g, 0.60 mmol) in methanol (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 green crystalline precipitate was filtered off and dried in the air. X-ray quality green crystals of *trans*-(Cl,Cl)-[Re(*p*-NC₆H₄CH₃)Cl₂(py-2-COO)(PPh₃)] (**1b**) and *cis*-(Cl,Cl)-[Re(*p*-NC₆H₄CH₃)Cl₂(py-2-COO)(PPh₃)] (**3**) were obtained by slow recrystallization from methanol. The crystals of **1b** and **3** were manually separated using microscope and they were collected in 25 and 65% yield, respectively. Both compounds crystallize in a monoclinic system (**1b** in Cc and **3** in P2₁/n space group), but they belong to different crystal classes, **1b** to monoclinic-domatic class, whereas **3** to prismatic crystal class. Different shapes and larger dimensions of the crystals **1b** facilitate hand-sorting of the crystals **1b** and **3**. The photos of the measured monocrystals of **1b** and **3** with their dimensions are shown in Scheme 5.

1b Cc space group; monoclinic-domatic class; 0.337 x 0.161 x 0.092 mm	3 P2 ₁ /n space group; prismatic crystal class; 0.113 x 0.048 x 0.022 mm

Scheme 5. The photos of the measured monocrystals of **1b** and **3**

trans-(Cl,Cl)-[Re(*p*-NC₆H₄CH₃)Cl₂(py-2-COO)(PPh₃)] (**1b**): IR (KBr; v/cm⁻¹): 3063(w), 1679(vs), 1641(sh), 1610(sh), 1590(m), 1564(sh), 1483(m), 1468(w), 1435(s), 1361(w), 1314(s), 1282(s), 1253(m), 1234(w), 1187(m), 1172(w), 1151(m), 1141(m), 1116(w),

1094(s), 1055(w), 1030(w), 1019(w), 853(s), 824(m), 768(m), 754(sh), 746(s), 709(s), 694(s), 674(s), 527(s), 510(m), 493(w), 456(w).

C₃₁H₂₆Cl₂N₂O₂Pre (746.61): calcd. C 49.87, H 3.51, N 3.75; found C 50.01, H 3.67, N 3.63%.

¹H NMR (DMSO, ppm): δ = 8.19(d, 1H, 7.7Hz), 8.07(td, 1H, 7.6Hz, 1.4Hz), 7.98(d, 1H, 5.4Hz), 7.92(ddd, 1H, 7.1Hz, 5.6Hz, 1.3Hz), 7.59(ddd, 6H, 9.8Hz, 7.7Hz, 1.7Hz), 7.49(dd, 7.4Hz, 2.0Hz, 9H), 7.42(d, 2H, 8.3Hz), 7.25(d, 8.2Hz, 2H and 2.26(s, 3H).

¹³C NMR (125 MHz, DMSO-d₆): δ = 169.2, 154.2, 148.2, 147.0, 143.0, 141.9, 134.6, 134.5, 131.8, 131.7, 131.5, 131.3, 128.9, 128.8, 121.9, 31.2, 22.4 ppm.

³¹P NMR (DMSO-d₆): δ = 25.57 ppm.

cis-(Cl,Cl)-[Re(*p*-NC₆H₄CH₃)Cl₂(py-2-COO)(PPh₃)] (3): IR (KBr; v/cm⁻¹): 3055(w), 2920(w) 1690(vs), 1607 (w), 1591(m), 1482(m), 1464(w), 1435(s), 1357(w), 1314(s), 1275(s), 1249(w), 1149(m), 1094(s), 1056(w), 1018(w), 857(m), 819(m), 752(m), 718(sh), 694(s), 559(w), 528(s), 455(w).

C₃₁H₂₆Cl₂N₂O₂Pre (746.61.53): calcd. C 49.87, H 3.51, N 3.75; found C 49.99, H 3.43, N 3.64%.

¹H NMR (DMSO, ppm): δ = 7.91 – 7.88(m, 1H), 7.72 – 7.61(m, 3H), 7.46 – 7.39(m, 9H), 7.33(td, 6H, 7.9Hz, 2.6Hz), 7.15(d, 2H, 8.1Hz), 7.04(d, 2H, 8.4Hz), 2.25(s, 3H).

¹³C NMR (125 MHz, DMSO-d₆): δ = 154.2, 152.9, 148.1, 146.2, 143.0, 141.9, 134.6, 134.5, 131.8, 131.5, 131.3, 131.0, 129.7, 129.3, 129.2, 129.1, 128.9, 128.8, 126.4, 125.9, 124.3, 121.9, 31.1, 22.4, 22.2 ppm.

³¹P NMR (DMSO-d₆): δ = 25.62 ppm.

Preparation of complexes 2 and 4

A procedure similar to that for **1b** and **3** was used with [Re(*p*-NC₆H₄CH₃)Br₃(PPh₃)₂] (0.52 g, 0.54 mmol), py-2-COOH (0.07 g, 0.60 mmol) and methanol (60 ml). Crystals *trans*-(Br,Br)-[Re(*p*-NC₆H₄CH₃)Br₂(py-2-COO)(PPh₃)] (**2**) and *cis*-(Br,Br)-[Re(*p*-NC₆H₄CH₃)Br₂(py-2-COO)(PPh₃)]·H₂O (**4**) were manually separated using microscope and they were collected in 30 and 60% yield, respectively. Both compounds crystallize in a monoclinic system (**3** in Cc and **4** in C2/c space group) but they belong to different crystal classes, **3** to monoclinic-domatic class, whereas **4** to prismatic crystal class. Different shapes and larger dimensions of crystals **2** additionally facilitate hand-sorting of the crystals. The photos of the measured monocrystals of **2** and **4** with their dimensions are shown in Scheme 6.

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<p style="text-align: center;">2</p> <p style="text-align: center;">Cc space group; monoclinic-domatic class; 0.249 x 0.133 x 0.019 mm</p>		<p style="text-align: center;">4</p> <p style="text-align: center;">C2/c space group; prismatic crystal class; 0.211 x 0.053 x 0.018 mm</p>		

Scheme 6. The photos of the measured monocrystals of 2 and 4

cis-(Br,Br)-[Re(*p*-NC₆H₄CH₃)Br₂(py-2-COO)(PPh₃)]·H₂O (4): IR (KBr; ν/cm^{-1}): 3063(w), 1682(vs), 1589(s), 1482(m), 1467(m), 1434(s), 1360(m), 1314(s), 1280(s), 1253(m), 1172(w), 1139(m), 1096(s), 1055(w), 1019(m), 852(m), 823(m), 766(sh), 744(s), 693(s), 574(w), 527(s), 508(m), 494(m) and 456(w).

C₃₁H₂₈Br₂N₂O₃Pre (853.54): calcd. C 43.62, H 3.31, N 3.28; found C 43.42, H 3.26, N 3.35%.

¹H NMR (DMSO, ppm): δ = 7.94(dd, 1H, 6.6Hz, 5.1Hz), 7.75 – 7.59(m, 4H), 7.51 – 7.39(m, 10H), 7.36 – 7.29(m, 5H), 7.17 – 7.11(m, 3H), 3.33(s, 2H) and 2.23(s, 3H).

¹³C NMR (125 MHz, DMSO-d₆): δ = 169.1, 156.5, 154.2, 148.2, 147.0, 143.0, 141.9, 134.6, 134.5, 134.1, 134.0, 131.8, 131.7, 131.5, 131.3, 129.8, 129.2, 129.1, 128.9, 128.8, 127.6, 126.6, 126.4, 125.9, 123.5, 122.9, 121.9, 118.6, 22.4 ppm.

³¹P NMR (DMSO-d₆): δ = 25.63 ppm.

Preparation of complexes 5 and 6

[Re(*p*-NC₆H₄CH₃)Cl₃(PPh₃)₂] (0.48 g, 0.54 mmol) or [Re(*p*-NC₆H₄CH₃)Br₃(PPh₃)₂] (0.52 g, 0.54 mmol) was refluxed in methanol (60 ml) for 4 h. The resulting solution was reduced in volume to ~10 ml and allowed to cool to room temperature. A brown crystalline precipitate of *trans*-[Re(*p*-NC₆H₄CH₃)Cl₂(OMe)(PPh₃)₂] (**5**) and *trans*-[Re(*p*-NC₆H₄CH₃)Br₂(OMe)(PPh₃)₂] (**6**) was filtered off and dried in the air. X-ray quality brown crystals of **5** and **6** were obtained by slow recrystallization from methanol, and collected in 80 and 85% yield, respectively.

trans-(Cl,Cl)-[Re(*p*-NC₆H₄CH₃)Cl₂(OMe)(PPh₃)₂] (5): IR (KBr; ν/cm^{-1}): 3055(w), 2897(w), 2804(w), 2094(w), 1586(w), 1571(w), 1481(m), 1434(s), 1337(w), 1315(sh), 1191(w), 1151(w), 1097(vs), 1029(w), 1014(w), 990(m), 822(m), 745(s), 706(sh), 693(s), 521(s), 512(sh), 499(sh), 443(m).

C₄₄H₄₀Cl₂NOP₂Re (917.81): calcd. C 57.58, H 4.39, N 1.53; found C 57.39, H 4.27, N 1.47%.

¹H NMR (DMSO, ppm): δ = 7.66 – 7.53 (m, 30H), 7.52 – 7.43(m, 2H), 7.31(d, 1H, 8.4Hz), 7.26(d, 1H, 8.4Hz), 3.17(s, 3H), 2.33(s, 3H).

¹³C NMR (125 MHz, DMSO-d₆): δ = 133.6, 132.7, 132.5, 131.9, 130.6, 129.3, 129.2, 123.5, 49.2, 21.0 ppm.

³¹P NMR (DMSO-d₆): δ = 25.62 ppm.

***trans*-(Br,Br)-[Re(*p*-NC₆H₄CH₃)Br₂(OMe)(PPh₃)₂] $\cdot\frac{1}{2}$ H₂O (6):** IR (KBr; v/cm⁻¹): 3054(w), 2905(w), 2807(w), 1593(w), 1571(w), 1481(m), 1433(s), 1332(w), 1313(sh), 1185(w), 1172(sh), 1149(w), 1090(vs), 1028(w), 1015(w), 995(m), 822(m), 745(s), 693(vs), 521(sh), 511(vs), 495(sh), 468(m), 445(m).

C₄₄H₄₂Br₂NO₂P₂Re (1016.74): calcd. C 51.97, H 4.16, N 1.38; found C 51.23, H 4.18, N 1.31%.

¹H NMR of **6** (DMSO, ppm): δ = 7.66 – 7.53 (m, 30H), 7.32(d, 2H, 8.1Hz), 7.27 – 7.24(m, 2H), 3.17(s, 3H), 3.54 (s, 1H) and 2.33(s, 3H).

¹³C NMR (125 MHz, DMSO-d₆): δ = 138.4, 132.5, 132.0, 131.9, 129.3, 129.2, 123.5, 49.0, 21.0 ppm.

³¹P NMR (DMSO-d₆): δ = 25.65 ppm.

Catalytic experiments

All reactions were performed using screw-cap tubes in a multi-reactor system. In a typical experiment: Aniline (**7a**, 0.5 mmol, 49 μ L) and ethyl diazoacetate (**8**, 0.5 mmol, 53 μ L) were added to a reactor tube containing the complex *cis*-[Re(*p*-NC₆H₄CH₃)Cl₂(py-2-COO)(PPh₃)] (2.5 mg, 0.0034 mmol, 0.68 mol%) without solvent and under argon. The reaction mixture was warmed to 70 °C and monitored by TLC and/or GLC until steady conversion of the starting materials. EtOAc (2 mL) was added to the resulting mixture, followed by filtration through celite and washing with additional EtOAc (4 mL). The solvent was evaporated at reduced pressure and the resulting reaction crude was purified by column chromatography (silica gel, hexane/EtOAc) to give the pure *N*-phenylglycine ethyl ester (**9a**) as a pale orange solid [39.4 mg, 71% yield (referred to the amount converted into **9a**)]. Compounds **9a–9c** were characterized by comparison of their physical and spectroscopic data with those reported in the literature.⁴

Computational Details

The gas phase geometries of *trans*-[Re(*p*-NC₆H₄CH₃)Cl₂(py-2-COO)(PPh₃)] and *cis*-[Re(*p*-NC₆H₄CH₃)Cl₂(py-2-COO)(PPh₃)] were optimized without any symmetry restrictions in singlet ground-states with the DFT method using GAUSSIAN-03 program package.²² The calculations were performed using three DFT methods (B3LYP, BP86, PBE1PBE) in combination with several basis sets.²³ The basis sets tested in this work are described in Table 2. The optimized geometries of *trans*-[Re(*p*-NC₆H₄CH₃)Cl₂(py-2-COO)(PPh₃)] and *cis*-[Re(*p*-NC₆H₄CH₃)Cl₂(py-2-COO)(PPh₃)] were verified by performing of frequency calculation. The absence of imaginary frequency ensures that the optimized geometries correspond to true energy minima. All the subsequent calculations were performed based on optimized geometries using PBE1PBE method in combination with the basis sets appointed in Table 3 as LTZ631+. Natural bond orbital (NBO) calculations were performed with the NBO code included in Gaussian03.²⁴

The electronic spectra were calculated with the TDDFT method and the solvent effect was simulated using the polarizable continuum model (PCM).²⁵

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Table 1. Crystal data and structure refinement for 1-6 complexes.

	1a	1b	2	3	4	5	6
Empirical formula	C ₃₃ H ₂₉ Cl ₂ N ₃ O ₂ PRe	C ₃ H ₂₆ Cl ₂ N ₂ O ₂ PRe	C ₃ H ₂₆ Br ₂ N ₂ O ₂ PRe	C ₃ H ₂₆ Cl ₂ N ₂ O ₂ PRe	C ₃ H ₂₈ Br ₂ N ₂ O ₃ PRe	C ₄₄ H ₄₀ Cl ₂ NOP ₂ Re	C ₄₄ H ₄₂ Br ₂ NO _{1.5} P ₂ Re
Formula weight [g·mol ⁻¹]	787.66	746.61	835.53	746.61	853.54	917.81	1016.74
Temperature [K]	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	triclinic
Space group	Pna2 ₁	Cc	Cc	P2 ₁ /h	C2/c	P-1	P-1
Unit cell dimensions [Å, °]	a = 22.0403(7) b = 9.7351(3) c = 14.5013(5)	a = 15.5583(7) b = 14.0916(8) c = 13.5172(7)	a = 15.7245(12) b = 14.0954(11) c = 13.5539(10)	a = 9.7816(5) b = 14.8808(8) c = 21.8833(14)	a = 41.1920(3) b = 8.0922(3) c = 21.8048(14)	a = 10.2167(3) b = 13.6809(4) c = 14.3814(4) α = 96.458(3) β = 92.186(2) γ = 98.091(3)	a = 10.5826(5) b = 13.5937(6) c = 14.4529(5) α = 87.048(3) β = 88.440(4) γ = 81.771(4)
Volume [Å ³]	3111.46(17)	2935.8(3)	2968.1(4)	3107.3(3)	6244.1(5)	1974.52(10)	2054.59(15)
Z	4	4	4	4	8	2	2
Density (calculated) [Mg/m ³]	1.681	1.689	1.870	1.596	1.816	1.544	1.642
Absorption coefficient [mm ⁻¹]	4.164	4.407	6.871	4.164	6.537	3.328	5.015
F(000)	1552	1464	1608	1464	3296	916	998
Crystal size [mm]	0.174 x 0.109 x 0.062	0.337 x 0.161 x 0.092	0.249 x 0.133 x 0.019	0.113 x 0.048 x 0.022	0.211 x 0.053 x 0.018	0.142 x 0.075 x 0.048	0.118 x 0.087 x 0.062
θ range for data collection [°]	3.47 to 25.00	3.46 to 24.99	3.44 to 24.99	3.34 to 25.00	3.45 to 25.00	3.39 to 25.00	3.36 to 25.00
Index ranges	-24 ≤ h ≤ 26 -9 ≤ k ≤ 11 -15 ≤ l ≤ 17	-18 ≤ h ≤ 17 -16 ≤ k ≤ 14 -16 ≤ l ≤ 15	-18 ≤ h ≤ 16 -14 ≤ k ≤ 16 -16 ≤ l ≤ 16	-10 ≤ h ≤ 11, -17 ≤ k ≤ 17, -25 ≤ l ≤ 24	-39 ≤ h ≤ 48 -9 ≤ k ≤ 9 -25 ≤ l ≤ 20	-12 ≤ h ≤ 11 -16 ≤ k ≤ 16 -17 ≤ l ≤ 17	-12 ≤ h ≤ 12 -16 ≤ k ≤ 16 -17 ≤ l ≤ 17
Reflections collected	20909	6955	6801	10922	15231	15600	20093
Independent reflections	5134 [R(int) = 0.0570]	4158 [R(int) = 0.0277]	4156 [R(int) = 0.0510]	5463 [R(int) = 0.0429]	5488 [R(int) = 0.0288]	6924 [R(int) = 0.0356]	7210 [R(int) = 0.0588]
Completeness to 2θ=25°	99.7%	99.7%	99.7%	99.7%	99.7%	99.8%	99.8%
Min. and max. transm.	0.485 and 1.000	0.608 and 1.000	0.396 and 1.000	0.655 and 1.000	0.530 and 1.000	0.709 and 1.000	0.507 and 1.000
Data/restraints/parameters	5134 / 0 / 381	4158 / 0 / 353	4156 / 0 / 353	5463 / 0 / 353	5488 / 0 / 365	6924 / 0 / 462	7210 / 0 / 480
Goodness-of-fit on F ²	1.084	1.164	1.021	0.988	1.021	0.997	1.011
Final R indices [I>2σ(I)]	R1 = 0.0411 wR2 = 0.1035	R1 = 0.0288 wR2 = 0.0911	R1 = 0.0433 wR2 = 0.0930	R1 = 0.0281 wR2 = 0.0549	R1 = 0.0298 wR2 = 0.0551	R1 = 0.0298 wR2 = 0.0583	R1 = 0.0380 wR2 = 0.0826
R indices (all data)	R1 = 0.0476 wR2 = 0.1074	R1 = 0.0332 wR2 = 0.0955	R1 = 0.0499 wR2 = 0.0987	R1 = 0.0443 wR2 = 0.0583	R1 = 0.0489 wR2 = 0.0591	R1 = 0.0389 wR2 = 0.0607	R1 = 0.0539 wR2 = 0.0901
Absolute structure parameter							
Largest diff. peak and hole [e Å ⁻³]	1.449 and -1.347	0.519 and -0.423	1.411 and -1.290	0.767 and -0.486	0.747 and -0.873	0.951 and -0.711	0.867 and -1.215

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Table 2. Basis sets employed for valence electrons of the complexes studied in this work. [View Article Online](#)
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Basis set	Re	N	O	C	H	Cl	P
LTZ631	LANL2TZ(f)	6-31G*	6-31G*	6-31G*	3-21+G*	6-31+G*	6-31+G*
LTZ6311	LANL2TZ(f)	6-31+G*	6-31+G*	6-31+G*	6-31+G*	6-31+G*	6-31+G*
LTZ631+	LANL2TZ(f)	6-31+G*	6-31+G*	6-31+G*	6-31++G**	6-31+G*	6-31+G*
LDZ631+	LANL2DZ	6-31+G*	6-31+G*	6-31G*	6-31+G**	6-31+G*	6-31+G*

Table 3. Atomic charges from the Natural Population Analysis (NPA) for **1** and **3** (PBE1PBE method in combination with LTZ631+).

Atom	1	3
Re(1)	0.075	0.052
N(1)	-0.380	-0.376
N(2)	-0.205	-0.221
O(1)	-0.635	-0.637
P(1)	1.327	1.340
Cl(1)	-0.308	-0.257
Cl(2)	-0.284	-0.223

Table 4. Wiberg bond index matrix in the NAO basis for **1** and **3** (PBE1PBE method in combination with LTZ631+).

Bond	1	3
Re(1)-N(1)	0.540	0.585
Re(1)-N(2)	2.087	2.060
Re(1)-O(1)	0.601	0.577
Re(1)-P(1)	0.781	0.762
Re(1)-Cl(1)	0.852	0.890
Re(1)-Cl(2)	0.878	0.929

Table 5. Reaction of aniline and ethyl diazoacetate catalyzed by rhenium complexes.^a

Entry	Catalyst	Solvent/atmosphere	Conversion (9a , 10a) (%) ^b
1	<i>trans</i> -Cl,Cl (1)	toluene (air)	-
2	<i>trans</i> -Cl,Cl (1)	neat (air)	17 (0)
3	<i>trans</i> -Cl,Cl (1)	neat (Ar)	42 (4)
4	<i>trans</i> -Br,Br (2)	neat (Ar)	53 (17)
5	<i>trans</i> -Br,Br (2) ^c	neat (Ar)	54
6	<i>trans</i> -Br,Br (2)	neat (Ar) ^d	17
7	<i>cis</i> -Cl,Cl (3)	neat (Ar)	62 (14)
8	<i>cis</i> -Cl,Cl (3)	neat (Ar) ^e	7
9	<i>cis</i> -Cl,Cl (3)	acetone (Ar)	- ^f
10	<i>cis</i> -Cl,Cl (3)	CH ₂ Cl ₂ (Ar)	17
11	<i>cis</i> -Cl,Cl (3)	CHCl ₃ (Ar)	19
12	<i>cis</i> -Cl,Cl (3)	MeOH (Ar)	10
13	<i>cis</i> -Cl,Cl (3)	MeCN (Ar)	5
14	<i>cis</i> -Cl,Cl (3)	MeNO ₂ (Ar)	23
15	<i>cis</i> -Cl,Cl (3)	DMF (Ar)	7
16	<i>cis</i> -Cl,Cl (3)	toluene (Ar)	5
17	<i>cis</i> -Cl,Cl (3) ^c	neat (Ar)	67 (12)
18	<i>cis</i> -Cl,Cl (3) ^c	neat (air)	19
19	<i>cis</i> -Br,Br (4)	neat (Ar)	54 (8)

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^a Reaction conditions: **7a** (0.5 mmol), **8** (0.5 mmol), Re complex (2.5 mg), solvent (2.0 mL), 70 °C, 24 h, unless otherwise stated. ^b Conversion into **9a** determined by GLC; the conversion into **10a** is given in parentheses. ^c 5.0 mg of the rhenium complex were used. ^d Reaction performed under microwave irradiation (30 W, 70 °C, 30 min) ^e Reaction carried out at rt. ^f The imine derived from acetone and aniline was formed quantitatively.

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Figure 1. The molecular structure of 1a, 1b, 2, 3 and 4. Displacement ellipsoids are drawn at 50% probability.

Figure 2. The molecular structure of **5** and **6**. Displacement ellipsoids are drawn at 50% probability.

Figure 3. Schematic representation of the energy levels with the partial frontier molecular orbital compositions of *trans*-(Cl,Cl)- and *cis*-(Cl,Cl)-[Re(*p*-NC₆H₄CH₃)Cl₂(py-2-COO)(PPh₃)].

Figure 4. The contours of selected HOMO and LUMO orbitals of *trans*-(Cl,Cl)- and *cis*-(Cl,Cl)-[Re(*p*-NC₆H₄CH₃)Cl₂(py-2-COO)(PPh₃)]. Positive values of the orbital contour are represented in red (0.04 au) and negative values – in green (–0.04 au).

Figure 5. The experimental (black) and calculated (red) electronic absorption spectra of **1** and **3**.