# Dalton Transactions

# PAPER

Cite this: DOI: 10.1039/c3dt52528g

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

Barbara Machura,\*<sup>a</sup> Izabela Gryca,<sup>a</sup> Jan Grzegorz Małecki,<sup>a</sup> Francisco Alonso\*<sup>b</sup> and Yanina Moglie<sup>b</sup>

Novel *p*-tolylimido rhenium(v) complexes *trans*-(Cl,Cl)-[Re(*p*-NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)Cl<sub>2</sub>(py-2-COO)(PPh<sub>3</sub>)]·MeCN (**1a**), *trans*-(Cl,Cl)-[Re(*p*-NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)Cl<sub>2</sub>(py-2-COO)(PPh<sub>3</sub>)] (**1b**), *trans*-(Br,Br)-[Re(*p*-NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)Br<sub>2</sub>(py-2-COO)(PPh<sub>3</sub>)] (**2**), *cis*-(Cl,Cl)-[Re(*p*-NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)Cl<sub>2</sub>(py-2-COO)(PPh<sub>3</sub>)] (**3**), *cis*-(Br,Br)-[Re(*p*-NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)-Br<sub>2</sub>(py-2-COO)(PPh<sub>3</sub>)]·H<sub>2</sub>O (**4**), *trans*-(Cl,Cl)-[Re(*p*-NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)Cl<sub>2</sub>(OMe)] (**5**) and *trans*-(Br,Br)-[Re(*p*-NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)Br<sub>2</sub>(OMe)(PPh<sub>3</sub>)<sub>2</sub>]·1/2H<sub>2</sub>O (**6**) were synthesized. The compounds were identified by elemental analysis, IR, NMR (<sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P), 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*-NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)Cl<sub>2</sub>(py-2-COO)(PPh<sub>3</sub>)]. In the first step, extended tests of the ability of different DFT methods (B3LYP, BP86, and 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*-NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)Cl<sub>2</sub>(py-2-COO)(PPh<sub>3</sub>)] were investigated at the TDDFT level employing the PBE1PBE functional. Additional information about bonding in the compounds [Re-(*p*-NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)Cl<sub>2</sub>(py-2-COO)(PPh<sub>3</sub>)] was obtained by NBO analysis. The catalytic activity of the complexes incorporating the picolinate ligand was studied and compared in the synthesis of *N*-substituted ethyl glycine esters from ethyl diazoacetate and amines.

Received 13th September 2013, Accepted 20th November 2013 DOI: 10.1039/c3dt52528g

www.rsc.org/dalton

# Introduction

The widespread contemporary interest in the coordination chemistry of rhenium arises mainly from the introduction of  $\beta^-$  emitting isotopes  $^{188}\text{Re}$  and  $^{186}\text{Re}$  in radiotherapy. There is still a need for fundamental knowledge about the structural and spectroscopic properties, redox activities, and the 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.<sup>2</sup> 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, which makes their handling easier for synthetic purposes. After the discovery by Toste that demonstrated the ability of the high-valent oxo-rhenium complex [ReIO<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] 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.<sup>3</sup> Espenson *et al.* found that methylrhenium trioxide (CH<sub>3</sub>ReO<sub>3</sub>) catalyzed the reaction of primary and secondary amines with ethyl diazoacetate to give *N*-substituted glycine ethyl esters.<sup>4</sup>

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  $[ReOX_3(PPh_3)_2]$  (X = Cl, Br) are excellent starting materials for the syntheses of these compounds and that the reaction course of  $[ReOX_3(PPh_3)_2]$  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  $[ReOX_2(N-O)(PPh_3)]$  and  $[ReOX(N-O)_2]$  might have a significant influence on their catalyst activity.<sup>5</sup>



View Article Online

<sup>&</sup>lt;sup>a</sup>Department of Crystallography, Institute of Chemistry, University of Silesia,

<sup>9</sup>th Szkolna St., 40-006 Katowice, Poland. E-mail: basia@ich.us.edu.pl

<sup>&</sup>lt;sup>b</sup>Departamento de Química Orgánica, Facultad de Ciencias, and Instituto de Síntesis Orgánica (ISO), Universidad de Alicante, Apdo. 99, 03080 Alicante, Spain. E-mail: falonso@ua.es

<sup>†</sup>Electronic supplementary information (ESI) available. CCDC 899354–899357 and 936243–936245. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt52528g

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 = Cl, 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  $\text{NR}^{2-}$  is isoelectronic to  $\text{O}^{2-}$  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 the Re(v) atom with halide ligands arranged in a *meridional* fashion and triphenyl-phosphine molecules *trans* located to each other.<sup>6</sup>

Herein, several novel imidorhenium(v) complexes, *trans*-(Cl,Cl)-[Re(*p*-NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)Cl<sub>2</sub>(py-2-COO)(PPh<sub>3</sub>)]·MeCN (1a), *trans*-(Cl,Cl)-[Re(*p*-NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)Cl<sub>2</sub>(py-2-COO)(PPh<sub>3</sub>)] (1b), *trans*-(Br,Br)-[Re(*p*-NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)Br<sub>2</sub>(py-2-COO)(PPh<sub>3</sub>)] (2), *cis*-(Cl,Cl)-[Re(*p*-NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)Cl<sub>2</sub>(py-2-COO)(PPh<sub>3</sub>)] (3), *cis*-(Br,Br)-[Re(*p*-NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)Br<sub>2</sub>(py-2-COO)(PPh<sub>3</sub>)] ·(4), *trans*-(Cl,Cl)-[Re(*p*-NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)Cl<sub>2</sub>(OMe)(PPh<sub>3</sub>)<sub>2</sub>] ·(5) and *trans*-(Cl,Cl)-[Re(*p*-NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)Br<sub>2</sub>(OMe)(PPh<sub>3</sub>)<sub>2</sub>]·1/2H<sub>2</sub>O (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*-NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)X<sub>2</sub>(py-2-COO)(PPh<sub>3</sub>)]. The catalytic activity of the complexes incorporating the 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-NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)Cl<sub>2</sub>(py-2-COO)- $(PPh_3)$ ]·MeCN (1a), trans-(Cl,Cl)-[Re(p-NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)Cl<sub>2</sub>(py-2-COO)(PPh<sub>3</sub>)] (1b), trans-(Br,Br)-[Re(p-NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)Br<sub>2</sub>(py-2-COO)- $(PPh_3)$ ] (2), cis-(Cl,Cl)-[Re(p-NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)Cl<sub>2</sub>(py-2-COO)(PPh<sub>3</sub>)] (3) and cis-(Br,Br)-[Re(p-NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)Br<sub>2</sub>(py-2-COO)(PPh<sub>3</sub>)]·H<sub>2</sub>O (4) were prepared by metathesis reactions between [Re(p- $NC_6H_4CH_3X_3(PPh_3)_2$  and the carboxylic ligand (Scheme 1). Interestingly, the reactions of  $[Re(p-NC_6H_4CH_3)X_3(PPh_3)_2]$  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 an 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)- $[Re(p-NC_6H_4CH_3)Cl_2(py-2-COO)(PPh_3)]$ ·MeCN (1a) and trans- $(Br,Br)-[Re(p-NC_6H_4CH_3)Br_2(py-2-COO)(PPh_3)]$  (2) when the reactions were carried out in acetonitrile. However, refluxing of  $[\text{Re}(p-\text{NC}_6\text{H}_4\text{CH}_3)X_3(\text{PPh}_3)_2]$  with py-2-COOH in methanol led



Scheme 1 Formation of complexes 1-6.

to a mixture of the compounds *trans*-(Cl,Cl)-[Re(*p*-NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)- $Cl_2(py-2-COO)(PPh_3)$ ] (1b) and  $cis-(Cl,Cl)-[Re(p-NC_6H_4CH_3) Cl_2(py-2-COO)(PPh_3)$ ] (3) for  $[Re(p-NC_6H_4CH_3)Cl_3(PPh_3)_2]$ , and trans-(Br,Br)-[Re(p-NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)Br<sub>2</sub>(py-2-COO)(PPh<sub>3</sub>)] (2) and cis-(Br,Br)-[Re(p-NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)Br<sub>2</sub>(py-2-COO)(PPh<sub>3</sub>)]·H<sub>2</sub>O (4) for  $[\text{Re}(p-\text{NC}_6\text{H}_4\text{CH}_3)\text{Br}_3(\text{PPh}_3)_2]$ . We anticipated that compounds  $[\text{Re}(p-\text{NC}_6\text{H}_4\text{CH}_3)X_3(\text{PPh}_3)_2]$  might react with methanol, exhibiting a different reactivity pattern from that in acetonitrile. As expected, the reactions of  $[\text{Re}(p-\text{NC}_6\text{H}_4\text{CH}_3)X_3(\text{PPh}_3)_2]$  with methanol afforded methoxy imido complexes trans-(Cl,Cl)- $[\operatorname{Re}(p-\operatorname{NC}_{6}\operatorname{H}_{4}\operatorname{CH}_{3})\operatorname{Cl}_{2}(\operatorname{OMe})(\operatorname{PPh}_{3})_{2}]$  (5) and trans-(Br,Br)- $[\operatorname{Re}(p-\operatorname{Re$  $NC_6H_4CH_3$  Br<sub>2</sub>(OMe)(PPh<sub>3</sub>)<sub>2</sub> · 1/2H<sub>2</sub>O (6) as a result of the replacement of the labile X ligand trans to the imido group with the methoxy ion coming from methanol. This behaviour is related to that observed for oxocomplexes  $[ReOX_3(PPh_3)_2]$  in which the X ligand trans to the oxo group is readily exchanged by the methoxy group giving  $[ReOX_2(OMe)(PPh_3)_2]^7$  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).

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. The 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<sup>2-</sup> is isoelectronic to O<sup>2-</sup> and tends to form analogous complexes with rhenium, a short comparison with Re(v) oxocompounds is worthwhile. The majority of the reported oxorhenium(v) complexes [ReOX<sub>2</sub>(N–O)(PPh<sub>3</sub>)] of uninegative bidentate N,O-chelating ligands have *cis*-arranged halide ions.<sup>8</sup> A rare *trans*-X,X conformation has been found in [ReCl<sub>2</sub>(APO)(PPh<sub>3</sub>)], [ReOCl<sub>2</sub>(DPO)(PPh<sub>3</sub>)],<sup>9</sup> [ReOX<sub>2</sub>(hbt)(PPh<sub>3</sub>)]<sup>4</sup> and [ReOX<sub>2</sub>(hpb)(PPh<sub>3</sub>)]<sup>4</sup> (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 [ReOX<sub>2</sub>(py-2-COO)(PPh<sub>3</sub>)] is concerned, only the *cis*-(X,X) isomers have been synthesized and characterized so far.<sup>10</sup>

For compounds  $[\text{Re}(\text{NAr})X_2(\text{N-O})(\text{PPh}_3)]$ , 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.<sup>11</sup> Calculations at the DFT level were undertaken for *trans*-(Cl,Cl)- and *cis*-(Cl,Cl)-[Re(*p*-NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)Cl<sub>2</sub>(py-2-COO)(PPh<sub>3</sub>)] to get a deeper insight into the structural, spectroscopic and bonding properties of isomeric forms.

### IR and <sup>1</sup>H NMR spectra

The IR spectra of **1a**, **1b**, **2**, **3** and **4** are dominated by very strong bands (at 1679 cm<sup>-1</sup> for **1a**, 1679 cm<sup>-1</sup> for **1b**, 1677 cm<sup>-1</sup> for **2**, 1690 cm<sup>-1</sup> for **3** and 1682 cm<sup>-1</sup> for **4**) assigned to  $\nu_{as}(CO_2)$  stretching mode. Strong  $\nu_s(CO_2)$  bands are found at 1313 and 1282 cm<sup>-1</sup> for **1a**·MeCN, 1314 and 1282 cm<sup>-1</sup> for **1b**, 1312 and 1287 cm<sup>-1</sup> for **2**, 1314 and

1278 cm<sup>-1</sup> for 3 and 1314 and 1280 cm<sup>-1</sup> for 4. High values of  $\Delta\nu(\text{CO}_2) = \nu_{as}(\text{CO}_2) - \nu_s(\text{CO}_2)$  (equal to  $\approx 350 \text{ cm}^{-1}$ ) reflect a unidentate coordination mode of the carboxylate group in the [Re(*p*-NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)X<sub>2</sub>(py-2-COO)(PPh<sub>3</sub>)] compounds.<sup>12</sup> For *trans*-(X,X) and *cis*-(X,X) isomers of [Re(*p*-NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)X<sub>2</sub>(py-2-COO)-(PPh<sub>3</sub>)], these absorptions are very similar and they are not distinctive for molecular structure determination. This conclusion was confirmed by calculations. The calculated  $\nu_{as}(\text{CO}_2)$  and  $\nu_s(\text{CO}_2)$  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<sup>-1</sup> for 1 and 1814, 1363 and 1336 cm<sup>-1</sup> for 3). In comparison with the experimental data, however, these values are shifted to higher frequencies by ~8%, which is a usual feature for this approach (Fig. S1†).

The calculated  $\nu$ (Re–NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>) frequencies appear at 1555, 1447 and 1063 cm<sup>-1</sup> for **1**, and 1555, 1453 and 1065 cm<sup>-1</sup> for **3**. Experimentally, these vibrations are difficult to identify as the  $\nu$ (Re–NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>) stretches are mixed with  $\nu$ <sub>C=N</sub> and  $\nu$ <sub>P-C</sub> modes of PPh<sub>3</sub> and py-2-COO<sup>-</sup> ligands.<sup>11</sup>

<sup>1</sup>H NMR spectra made it possible to distinguish between *cis* and *trans* stereoisomers of  $[\text{Re}(p\text{-NC}_6\text{H}_4\text{CH}_3)\text{X}_2(\text{py-2-COO})-(\text{PPh}_3)]$  (Fig. 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 the 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 the 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 the 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  $[\text{Re}(p\text{-NC}_6\text{H}_4\text{CH}_3)X_2(\text{OMe})(\text{PPh}_3)_2]$  was additionally confirmed by <sup>31</sup>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;† Fig. 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 the PPh<sub>3</sub> 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 the *trans* position to the *p*-methylphenylimido ion. This occupancy is justified by the *trans*-influence of the imido group forcing harder the oxygen atom of the N–O ligand into the *trans* position. Triphenylphosphine molecule with its  $\pi$ -acidity adopts a *cis* disposition with respect to the linear RN≡Re–O core and stabilizes it due

		,				1	
	1a	1b	2	3	4	5	9
Empirical formula Formula weight	C <sub>33</sub> H <sub>29</sub> Cl <sub>2</sub> N <sub>3</sub> O <sub>2</sub> PRe 787.66	C <sub>31</sub> H <sub>26</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>2</sub> PRe 746.61	C <sub>31</sub> H <sub>26</sub> Br <sub>2</sub> N <sub>2</sub> O <sub>2</sub> PRe 835.53	C <sub>31</sub> H <sub>26</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>2</sub> PRe 746.61	C <sub>31</sub> H <sub>28</sub> Br <sub>2</sub> N <sub>2</sub> O <sub>3</sub> PRe 853.54	C <sub>44</sub> H <sub>40</sub> Cl <sub>2</sub> NOP <sub>2</sub> Re 917.81	$C_{44}H_{42}Br_2NO_{1.5}P_2Re$ 1016.74
lg moi J Temperature [K] Wavelength [Å] Crystal system	293(2) 0.71073 Orthorhombic	293(2) 0.71073 Monoclinic	293(2) 0.71073 Monoclinic	293(2) 0.71073 Monoclinic	293(2) 0.71073 Monoclinic	293(2) 0.71073 Triclinic	293(2) 0.71073 Triclinic
opace group Unit cell dimensions [Å,°]	$ \begin{array}{l} r^{102,1}\\ a=22.0403(7)\\ b=9.7351(3)\\ c=14.5013(5) \end{array} \end{array} $	$cc = 15.5583(7) \\ a = 15.5583(7) \\ b = 14.0916(8) \\ c = 13.5172(7)$	$cc = 15.7245(12) \\ b = 14.0954(11) \\ c = 13.5539(10) \\ c = 13.5599(10) \\ c = 13.59$	$p_{r-1,l,m}$ a = 9.7816(5) b = 14.8808(8) c = 21.8833(14)	$C_{2/C}$ a = 41.1920(3) b = 8.0922(3) c = 21.8048(14)	$ \begin{array}{l} r_1 \\ a = 10.2167(3) \\ b = 13.6809(4) \\ c = 14.3814(4) \end{array} \end{array} $	$ \begin{array}{l} p_1 \\ a = 10.5826(5) \\ b = 13.5937(6) \\ c = 14.4529(5) \\ \end{array} $
		eta=97.838(4)	eta=98.885(7)	eta=102.709(6)	$\beta = 120.786(9)$	$\alpha = 96.458(3)$ $\beta = 92.186(2)$	$\alpha = 87.048(3)$ $\beta = 88.440(4)$
Volume [ų]	3111.46(17)	2935.8(3)	2968.1(4)	3107.3(3)	6244.1(5)	$\gamma = 98.091(3)$ 1974.52(10)	$\gamma = 81.71(4)$ 2054.59(15)
ے Density (calculated)	$^{4}$ 1.681	$^{4}$ 1.689	$\frac{4}{1.870}$	$\frac{4}{1.596}$	。 1.816	$^{2}$ 1.544	$^{2}$ 1.642
[Mg m ~] Absorption coefficient [ <sup>1</sup> 1	4.164	4.407	6.871	4.164	6.537	3.328	5.015
[uuu ] F(000] Crvstal size [mm]	1552 0.174 × 0.109 × 0.062	1464 0.337 × 0.161 × 0.092	$\begin{array}{c} 1608 \\ 0.249 \times 0.133 \times 0.019 \end{array}$	$\begin{array}{c} 1464 \\ 0.113 \times 0.048 \times 0.022 \end{array}$	3296 0.211 × 0.053 × 0.018	916 0.142 × 0.075 × 0.048	998 $0.118 \times 0.087 \times 0.062$
$\theta$ range for data collection $[\circ]$	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	$-24 \le h \le 26 - 9 \le k \le 11 - 15 \le l \le 17$	$-18 \le h \le 17 - 16 \le k \le 14 - 16 \le l \le 15$	$-18 \le h \le 16 - 14 \le k \le 16 - 16 \le l \le 16$	$-10 \le h \le 11, -17 \le k \le 17, -25 \le l \le 24$	$-39 \le h \le 48 - 9 \le k < 9 - 25 < l < 20$	$-12 \le h \le 11 - 16 \le k \le 16 - 17 \le l \le 17$	$-12 \le h \le 12 - 16 \le k \le 16 - 17 \le l \le 17$
Reflections collected Independent reflections Completeness to	$20_{99} - \frac{20_{99}}{5134} \left[ R(\text{int}) = 0.0570 \right]$	$\begin{array}{c} 6955 \\ 4158 \left[ R(\text{int}) = 0.0277 \right] \\ 99.7\% \end{array}$	68014156 [R(int) = 0.0510]99.7%	$\begin{array}{c} 10.922 \\ 5463 \left[ R(\text{int}) = 0.0429 \right] \\ 99.7\% \end{array}$	152315488 [R(int) = 0.0288]99.7%	$15600 \\ 6924 \left[ R(int) = 0.0356 \right] \\ 99.8\%$	20093 7210 [R(int) = 0.0588] 99.8%
20 = 25° Min. and max. transm. Data/restraints/	0.485 and 1.000 5134/0/381	0.608 and 1.000 4158/0/353	0.396 and 1.000 4156/0/353	0.655 and 1.000 5463/0/353	0.530 and 1.000 5488/0/365	0.709 and 1.000 6924/0/462	0.507 and 1.000 7210/0/480
parameters Goodness-of-fit on $F^2$	1.084	1.164	1.021	0.988	1.021	0.997	1.011
Final R indices $[I > 2n(I)]$	$R_1 = 0.0411$ w $R_2 = 0.1035$	$R_1 = 0.0288$ wR <sub>2</sub> = 0.0911	$R_1 = 0.0433$ wR <sub>2</sub> = 0.0930	$R_1 = 0.0281$ w $R_2 = 0.0549$	$R_1 = 0.0298$ w $R_2 = 0.0551$	$R_1 = 0.0298$ w $R_2 = 0.0583$	$R_1 = 0.0380$ w $R_2 = 0.0826$
R indices (all data)	$R_1 = 0.0476$ w $R_2 = 0.1074$	$R_1 = 0.0332$ w $R_2 = 0.0955$	$R_1 = 0.0499$ w $R_2 = 0.0987$	$R_1 = 0.0443$ w $R_2 = 0.0583$	$R_1 = 0.0489$ w $R_2 = 0.0591$	$R_1 = 0.0389$ w $R_2 = 0.0607$	$R_1 = 0.0539$ wR <sub>2</sub> = 0.0901
Absolute structure	7.1.1	-0.013(10)	7.1	200000 7	7 00000 7 11	7	70000 7.11
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 -1.218

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

Paper



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



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

to accessible  $\pi$ -donation from rhenium to the PPh<sub>3</sub> 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 [Re(*p*-NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)X<sub>2</sub>(py-2-COO)(PPh<sub>3</sub>)]. The Re-N<sub>imido</sub>-C<sub>imido</sub> bond angles of 167.9(6)° in **1a**, 171.9(10)° in **1b**, 173.1(10)° in **2**, 174.4(3)° in **3** and 175.1(3)° in **4** agree with a linear coordination mode of the arylimido ligands (167–176°), and these values are typical of phenyl imido ligands in high oxidation state complexes, in which the metal is relatively electron-deficient and some  $\pi$ -bonding between the imido nitrogen atom and the metal exist. The Re–N<sub>imido</sub> 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 [Re $\equiv$ NR]<sup>3+</sup> core, and reflect the expected triple Re $\equiv$ N bond.<sup>6,11</sup> The interatomic distance between the rhenium atom and the

carboxylate oxygen atom is almost equal to an ideal single Re– O bond length (*ca.* 2.04 Å),<sup>13</sup> indicating lack of delocalization in the RN $\equiv$ Re–O unit.

The complexes **5** and **6** were found to be *trans*-(X,X) isomers with the methoxy ligand *trans* to the Re $\equiv$ NR moiety. The elongation of the Re–N<sub>imido</sub> (in comparison with the corresponding values for **1**–4) is accompanied by a shortening of the Re–O distance *trans* to the Re $\equiv$ NR moiety. It is a consequence of the competition of the methoxy ion with the imido group in the interaction with the d $\pi$  orbitals of the metal. The Re–OCH<sub>3</sub> distances in **5** [1.915(3) Å] and **6** [1.898(3) Å] indicate a significant double-bond character.<sup>14</sup> The larger delocalization of electron density in the linear RN $\equiv$ Re–OCH<sub>3</sub> core results in a less pronounced electron transfer by  $\pi$  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, and PBE1PBE) to find the best overall performer in describing the geometry of the imido Re(v) complexes were performed. The geometries of *trans*-(Cl,Cl)-[Re(*p*-NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)Cl<sub>2</sub>(py-2-COO)(PPh<sub>3</sub>)] and *cis*-(Cl,Cl)-[Re(*p*-NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)Cl<sub>2</sub>(py-2-COO)(PPh<sub>3</sub>)] were optimized in singlet states using three DFT methods (B3LYP, BP86, and PBE1PBE) in combination with several basis sets given in Table 2.

All the methods give acceptable deviations between the experimental and theoretical geometric data. The largest deviations were found for the BP86 procedure, whereas both geometries were best reproduced by employing the PBE1PBE method (Table S2<sup>†</sup>). It gives an excellent estimation of Re-N<sub>imido</sub> bond lengths with deviations smaller than 0.003 Å. Deviations of the distance Re-N<sub>imido</sub> for the methods B3LYP, and BP86 are larger, from 0.009 to 0.014 Å for B3LYP, and from 0.030 to 0.033 Å for BP86 (Fig. S3<sup>†</sup>). The Re-N<sub>py</sub> and Re-O bond lengths are also well reproduced with errors ranging from -0.004 to -0.035 Å for Re-N<sub>py</sub> 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.<sup>15</sup> This issue can be partly solved using the dispersion corrected functional in the DFT method, as indicated by the results for the dispersion corrected B3LYP

functional (Table S2<sup>†</sup>). Further calculations were performed using the PBE1PBE method in combination with the basis sets presented in Table 2 as LTZ631+.

For both compounds, the calculated charge on the rhenium atom is considerably 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**.

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 the *cis*-(Cl,Cl)-[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  $\sigma$  and two  $\pi$ natural Re–N<sub>imido</sub> orbitals. Both  $\sigma$  and  $\pi$  bonds are strongly polarized towards the nitrogen atom. The hybridization at rhenium shows clearly that d contribution dominates the metal bonding in  $\sigma$  and  $\pi$  Re–N<sub>imido</sub> bonds. For  $\pi$  bonds the nitrogen atom of the imido ligand employs pure or quasi pure p atomic orbitals (Fig. S4b†).

For the *trans*-(Cl,Cl) isomer, two Re–N<sub>imido</sub> 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  $\pi$  character (Fig. S4a†). Lack of  $\sigma_{Re-NR}$  natural orbital indicates a conceivable predominant Coulomb-type Re–ligand interaction.<sup>16</sup> The nature of Re–N<sub>imido</sub> bonds is in agreement with the results obtained in previous studies regarding the analysis of the bonding nature of rhenium imido complexes.<sup>5,11</sup>

Table 3Atomic charges from the Natural Population Analysis (NPA) for1 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 2
 Basis sets employed for valence electrons of the complexes studied in this work

Basis set	Re	Ν	0	С	Н	Cl	Р
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 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

The triple bond character of Re– $N_{\rm imido}$  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 Re(1)–N(2) are over three times larger than those of Re(1)–N(1) in 1 and Re(1)–N(1) in 3.

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  $(1.92-3.74 \text{ kcal mol}^{-1})$ , indicating that their formation is kinetically rather than thermodynamically controlled.

A schematic representation of the energy levels with the partial frontier molecular orbital compositions of **1** and **3** is presented in Fig. 3. The contours of the selected frontier orbitals are depicted in Fig. 4. As can be seen from Fig. 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 the *cis*-(Cl,Cl) isomer, this molecular orbital is also insignificantly contributed by the 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  $d_{\pi}$  orbital (14% for 1 and 13% for 3). To a large extent, the HOMO-1 of 1 and 3 can be considered as  $\pi_{Re=NR}$ orbital. For the *cis*-(Cl,Cl) isomer, a moderate contribution from the antibonding interaction of rhenium  $d_{\pi}$  orbital with Cl orbitals (12%) is also 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  $\pi^*$ -antibonding orbital and the d<sub> $\pi$ </sub> rhenium orbital. A significant contribution of  $\pi^*_{Re=NR}$  orbitals is also observed in LUMO+1 and LUMO+2 of **1** and **3**, unlike LUMO, however, these MOs are predominantly localized on the  $\pi^*$ -antibonding orbitals of the picolinate ligand.

By comparing the FMO energy levels of 1 and 3, an insignificant increase in the energy gap HOMO–LUMO for the *cis*-(Cl,

Cl) isomer (3.28 for 1 and 3.46 eV 3) can be found. For this geometry, the energy level of HOMO level is stabilized whereas the energy level of LUMO is slightly raised compared with complex 1.

#### **Electronic spectra**

The complexes **1** and **3** have similar absorption character and TDDFT transitions well correlate with the experimental absorptions, as illustrated in Fig. 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  $\rightarrow$  LUMO and HOMO  $\rightarrow$  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 $\rightarrow$ d (*Ligand Field*; *LF*), d $\pi$ (Cl) $\rightarrow$ d<sub>Re</sub> (*Ligand–Metal Charge Transfer*; *LMCT*) and  $\pi$ (Cl) $\rightarrow$  $\pi^*(p$ -tol)/ $\pi^*$ (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 correlates well with the increase in 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  $\rightarrow$  LUMO+2 transition can be seen as mixed d $\rightarrow$ d,  $\pi$ (Cl) $\rightarrow$ d<sub>Re</sub>, d<sub>Re</sub> $\rightarrow \pi^{*}$ (py-2-COO)/ $\pi^{*}$ (*p*-tol) and  $\pi$ (Cl) $\rightarrow \pi^{*}$ (py-2-COO)/ $\pi^{*}$ (*p*-tol) transitions. The intense bands in the 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.<sup>4</sup> 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).

Initial studies with the complex trans-Cl,Cl (1) at 70 °C under air, either in toluene or without a 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 a 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 the amount of the catalyst was utilized (Table 5, entry 5), whereas microwave irradiation did not have any influence on the reaction rate (Table 5, entry 6). Higher conversion was achieved for 9a with cis-Cl,Cl (3) under solvent-free conditions, which was formed together with minor amounts of 10a (Table 5, entry 7). Reactions with cis-Cl,Cl (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-Cl,Cl (3), with concomitant formation of 10a (Table 5, compare entries 7 and 17). Under the



Fig. 3 Schematic representation of the energy levels with the partial frontier molecular orbital compositions of trans-(Cl,Cl)- and cis-(Cl,Cl)-[Re(p-NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)Cl<sub>2</sub>(py-2-COO)(PPh<sub>3</sub>)].

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*-Cl,Cl (1) (Table 5, entries 1 and 2). Finally, *cis*-Br,Br (4) behaved similar to *trans*-Br,Br (2) (Table 5, compare entries 4 and 19), with the stereochemistry of the complexes having no apparent effect on 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*-Cl,Cl-[Re]



Fig. 4 The contours of selected HOMO and LUMO orbitals of *trans*-(Cl,Cl)- and *cis*-(Cl,Cl)-[Re(p-NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)Cl<sub>2</sub>(py-2-COO)(PPh<sub>3</sub>)]. Positive values of the orbital contour are represented in red (0.04 au) and negative values in green (-0.04 au).

(3) was shown to be superior in the latter reaction (9c, 95% yield) when compared with the other complexes studied, namely, *trans*-Cl,Cl-[Re] (1) (9c, 31% yield), *trans*-Br,Br-[Re] (2) (9c, 53% yield), and *cis*-Br,Br-[Re] (4) (9c, 19% yield).

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.<sup>17</sup> 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



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



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

Entry	Catalyst	Solvent/ atmosphere	Conversion <sup><math>b</math></sup> (9a, 10a) (%)
1	trans-Cl.Cl (1)	Toluene (air)	
2	trans-Cl.Cl (1)	Neat (air)	17 (0)
3	trans-Cl,Cl (1)	Neat (Ar)	42 (4)
4	trans-Br,Br (2)	Neat (Ar)	53 (17)
5	trans-Br, Br $(2)^{c}$	Neat (Ar)	54
6	trans-Br,Br (2)	Neat $(Ar)^d$	17
7	cis-Cl,Cl (3)	Neat (Ar)	62 (14)
8	cis-Cl,Cl (3)	Neat $(Ar)^e$	7
9	cis-Cl,Cl (3)	Acetone (Ar)	f
10	cis-Cl,Cl (3)	$CH_2Cl_2$ (Ar)	17
11	cis-Cl,Cl (3)	CHCl <sub>3</sub> (Ar)	19
12	cis-Cl,Cl (3)	MeOH (Ar)	10
13	cis-Cl,Cl (3)	MeCN (Ar)	5
14	cis-Cl,Cl (3)	$MeNO_2$ (Ar)	23
15	cis-Cl,Cl (3)	DMF (Ar)	7
16	cis-Cl,Cl (3)	Toluene (Ar)	5
17	cis-Cl,Cl (3) <sup>c</sup>	Neat (Ar)	67 (12)
18	$cis$ -Cl,Cl $(3)^{c}$	Neat (air)	19
19	cis-Br,Br (4)	Neat (Ar)	54 (8)

 
 Table 5
 Reaction of aniline and ethyl diazoacetate catalyzed by rhenium complexes<sup>a</sup>

<sup>*a*</sup> 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. <sup>*b*</sup> Conversion into **9a** determined by GLC; the conversion into **10a** is given in parentheses. <sup>*c*</sup> 5.0 mg of the rhenium complex were used. <sup>*d*</sup> Reaction performed under microwave irradiation (30 W, 70 °C, 30 min). <sup>*e*</sup> Reaction carried out at rt. <sup>*f*</sup> The imine derived from acetone and aniline was formed quantitatively.



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

carbon atom of the metallacycle.<sup>4</sup> In our case, the scenario is rather different as no Re $\equiv$ 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



Scheme 4 Proposed reaction mechanism.

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 considerably 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.

A comparison between the reactivity of the complexes 1–4 seems more difficult to establish. On the 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  $\sigma$  and two  $\pi$  bonds of Re–N<sub>imido</sub> in *cis*-(Cl,Cl) strongly polarized towards the nitrogen atom, and the lack of  $\sigma_{\text{Re-NR}}$  natural orbital in *trans*-(Cl,Cl), which 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 PPh<sub>3</sub> is the ligand exchanged by the carbene derived from ethyl diazoacetate (we always detect some PPh<sub>3</sub> as a byproduct),<sup>18</sup> this exchange could be more favoured for a certain stereochemistry on the basis of steric factors or the strength of the interaction of PPh<sub>3</sub> with the metal. On this basis, PPh<sub>3</sub> might interact more strongly 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 MeReO<sub>3</sub>, produced compound **9a** in a higher yield (89%) under milder reaction conditions, the long reaction times applied and the use of dry benzene as a solvent curtail its practical application.<sup>4</sup> 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  $[\text{Re}(p-\text{NC}_6\text{H}_4\text{CH}_3)\text{Cl}_3(\text{PPh}_3)_2]$  (X = Cl, Br) towards pyridine-2-carboxylic acid has been examined and compared with the related exchange reactions performed with oxocompounds  $[ReOX_3(PPh_3)_2]$ . 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-NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)X<sub>2</sub>(py-2-COO)(PPh<sub>3</sub>)] and cis-(X,X)- $[Re(p-NC_6H_4CH_3)X_2(py-2-COO)(PPh_3)],$  the pyridine-2-carboxylate ion is coordinated in a chelate way via N- and O-donor atoms, and the PPh<sub>3</sub> 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. The X-ray studies and NBO analysis confirm a linear coordination mode of the *p*-NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub> ligand and the 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 solventfree conditions. The complex cis-(Cl,Cl)-[Re(p-NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)-Cl<sub>2</sub>(py-2-COO)(PPh<sub>3</sub>)] (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 sideproduct. 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-[Re(p-NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)X<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>] (X = Cl, Br) were prepared according to the literature methods.<sup>19</sup>

#### Instrumentation

IR spectra were recorded on a Nicolet Magna 560 spectrophotometer in the spectral range 4000–400 cm<sup>-1</sup> with the samples in the form of KBr pellets. The <sup>1</sup>H NMR, <sup>13</sup>C NMR and <sup>31</sup>P

NMR spectra were recorded (298 K) on a Bruker Avance 500 NMR spectrometer at a resonance frequency of 500 MHz for <sup>1</sup>H NMR spectra, 125 MHz for <sup>13</sup>C NMR spectra and 162 MHz for <sup>31</sup>P NMR using DMSO-d<sub>6</sub> as a 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 an Atlas CCD detector and graphite monochromated  $MoK_{\alpha}$  radiation ( $\lambda = 0.71073$  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 were applied.<sup>20</sup> 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 a full-matrix, least-squares technique. The hydrogen atoms were treated as "riding" on their parent carbon atoms and assigned isotropic temperature factors equal to 1.2 (non-methyl) and 1.5 (methyl) times the value of the 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.<sup>21</sup> 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.

### Preparation of complexes 1a and 2

*mer*-[Re(*p*-NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)Cl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>] (0.43 g, 0.54 mmol) or [Re(*p*-NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)Br<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>] (0.52 g, 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*-NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)Cl<sub>2</sub>(py-2-COO)-(PPh<sub>3</sub>)]·MeCN (1a) or *trans*-(Br,Br)-[Re(*p*-NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)Br<sub>2</sub>(py-2-COO)(PPh<sub>3</sub>)] (2) was filtered off and dried in 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-NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)Cl<sub>2</sub>(py-2-COO)(PPh<sub>3</sub>)]·MeCN (1a). IR (KBr;  $\nu$ /cm<sup>-1</sup>): 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).

 $C_{33}H_{29}Cl_2N_3O_2PRe$  (787.66): calcd C 50.32, H 3.71, N 5.33; found C 50.59, H 3.62, N 5.24%.

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

<sup>13</sup>C NMR: 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.

<sup>31</sup>P NMR: 25.58 ppm.

*trans*-(**Br**,**Br**)-[**Re**(*p*-**N**C<sub>6</sub>**H**<sub>4</sub>**CH**<sub>3</sub>)**Br**<sub>2</sub>(**py**-**2**-**COO**)(**PPh**<sub>3</sub>)] (2). IR (KBr;  $\nu/\text{cm}^{-1}$ ): 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).

 $C_{31}H_{26}Br_2N_2O_2PRe$  (835.53): calcd C 44.56, H 3.14, N 3.35; found C 44.83, H 3.19, N 3.38%.

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

<sup>13</sup>C NMR: 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.

<sup>31</sup>P NMR: 25.65 ppm.

#### Preparation of complexes 1b and 3

 $[\operatorname{Re}(p-\operatorname{NC}_6\operatorname{H}_4\operatorname{CH}_3)\operatorname{Cl}_3(\operatorname{PPh}_3)_2]$  (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 air. X-ray quality green crystals of trans-(Cl,Cl)-[Re(p-NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)Cl<sub>2</sub>(py-2-COO)(PPh<sub>3</sub>)] (1b) and cis-(Cl,Cl)-[Re(p-NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)Cl<sub>2</sub>(py-2-COO)(PPh<sub>3</sub>)] (3) were obtained by slow recrystallization from methanol. The crystals of 1b and 3 were manually separated using a microscope and they were collected in 25 and 65% yield, respectively. Both compounds crystallize in a monoclinic system (1b in Cc and 3 in  $P2_1/n$  space group), but they belong to different crystal classes, 1b to the monoclinic-domatic class, whereas 3 belongs to the 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 Fig. 6.

*trans*-(Cl,Cl)-[Re(*p*-NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)Cl<sub>2</sub>(py-2-COO)(PPh<sub>3</sub>)] (1b). IR (KBr;  $\nu$ /cm<sup>-1</sup>): 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), 527(s), 510(m), 493(w), 456(w).



Fig. 6 The photos of the measured monocrystals of 1b and 3.

Paper

 $C_{31}H_{26}Cl_2N_2O_2PRe~(746.61)\text{: calcd C } 49.87,~H~3.51,~N~3.75; found~C~50.01,~H~3.67,~N~3.63\%.$ 

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

<sup>13</sup>C NMR: 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.

<sup>31</sup>P NMR: 25.57 ppm.

 $C_{31}H_{26}Cl_2N_2O_2PRe \ \ (746.61.53): \ \ calcd \ \ C \ \ 49.87, \ \ H \ \ 3.51, \\ N \ 3.75; \ found \ C \ \ 49.99, \ H \ 3.43, \ N \ 3.64\%.$ 

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

<sup>13</sup>C NMR: 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.

<sup>31</sup>P NMR: 25.62 ppm.

### Preparation of complexes 2 and 4

A procedure similar to that for **1b** and **3** was used with  $[\text{Re}(p-\text{NC}_6\text{H}_4\text{CH}_3)\text{Br}_3(\text{PPh}_3)_2]$  (0.52 g, 0.54 mmol), py-2-COOH (0.07 g, 0.60 mmol) and methanol (60 ml). Crystals of *trans*-(Br,Br)- $[\text{Re}(p-\text{NC}_6\text{H}_4\text{CH}_3)\text{Br}_2(\text{py-2-COO})(\text{PPh}_3)]$  (2) and *cis*-(Br,Br)- $[\text{Re}(p-\text{NC}_6\text{H}_4\text{CH}_3)\text{Br}_2(\text{py-2-COO})(\text{PPh}_3)]\cdot\text{H}_2\text{O}$  (4) were manually separated using a microscope and 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** belongs to the 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 Fig. 7.



Fig. 7 The photos of the measured monocrystals of 2 and 4.

 $cis\mbox{-}(Br,Br)\mbox{-}[Re(p\mbox{-}NC_6H_4CH_3)Br_2(py\mbox{-}2\mbox{-}COO)(PPh_3)]\mbox{-}H_2O$  (4). IR (KBr;  $\nu/\mbox{cm}^{-1}$ ): 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).

 $C_{31}H_{28}Br_2N_2O_3PRe$  (853.54): calcd C 43.62, H 3.31, N 3.28; found C 43.42, H 3.26, N 3.35%.

<sup>1</sup>H NMR: 7.94(dd, 1H, 6.6 Hz, 5.1 Hz), 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) ppm.

<sup>13</sup>C NMR: 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.

<sup>31</sup>P NMR: 25.63 ppm.

#### Preparation of complexes 5 and 6

 $[\operatorname{Re}(p\operatorname{-NC}_{6}\operatorname{H}_{4}\operatorname{CH}_{3})\operatorname{Cl}_{3}(\operatorname{PPh}_{3})_{2}] (0.48 \text{ g, } 0.54 \text{ mmol}) \text{ or } [\operatorname{Re}(p\operatorname{-NC}_{6}\operatorname{H}_{4}\operatorname{CH}_{3})\operatorname{Br}_{3}(\operatorname{PPh}_{3})_{2}] (0.52 \text{ g, } 0.54 \text{ mmol}) \text{ was refluxed in methanol } (60 \text{ ml}) \text{ for 4 h. The resulting solution was reduced in volume to ~10 ml and allowed to cool to room temperature. A brown crystalline precipitate of$ *trans* $-[\operatorname{Re}(p\operatorname{-NC}_{6}\operatorname{H}_{4}\operatorname{CH}_{3})\operatorname{-Cl}_{2}(\operatorname{OMe})(\operatorname{PPh}_{3})_{2}] (5) \text{ and } trans-[\operatorname{Re}(p\operatorname{-NC}_{6}\operatorname{H}_{4}\operatorname{CH}_{3})\operatorname{Br}_{2}(\operatorname{OMe}) (\operatorname{PPh}_{3})_{2}] (6) \text{ was filtered off and dried in air. X-ray quality brown crystals of 5 and 6 were obtained by slow recrystallization from methanol, and collected in 80 and 85% yield, respectively.$ 

*trans*-(Cl,Cl)-[Re(*p*-NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)Cl<sub>2</sub>(OMe)(PPh<sub>3</sub>)<sub>2</sub>] (5). IR (KBr;  $\nu/cm^{-1}$ ): 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).

 $C_{44}H_{40}Cl_2NOP_2Re$  (917.81): calcd C 57.58, H 4.39, N 1.53; found C 57.39, H 4.27, N 1.47%.

<sup>1</sup>H NMR: 7.66–7.53(m, 30H), 7.52–7.43(m, 2H), 7.31(d, 1H, 8.4 Hz), 7.26(d, 1H, 8.4 Hz), 3.17(s, 3H), 2.33(s, 3H) ppm.

<sup>13</sup>C NMR: 133.6, 132.7, 132.5, 131.9, 130.6, 129.3, 129.2, 123.5, 49.2, 21.0 ppm.

<sup>31</sup>P NMR: 25.62 ppm.

*trans*-(**Br**,**Br**)-[**Re**(p-**NC**<sub>6</sub>**H**<sub>4</sub>**CH**<sub>3</sub>)**Br**<sub>2</sub>(**OMe**)(**PPh**<sub>3</sub>)<sub>2</sub>]·**1**/2**H**<sub>2</sub>**O** (6). IR (KBr;  $\nu/\text{cm}^{-1}$ ): 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).

C<sub>44</sub>H<sub>42</sub>Br<sub>2</sub>NO<sub>2</sub>P<sub>2</sub>Re (1016.74): calcd C 51.97, H 4.16, N 1.38; found C 51.23, H 4.18, N 1.31%.

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

<sup>13</sup>C NMR: 138.4, 132.5, 132.0, 131.9, 129.3, 129.2, 123.5, 49.0, 21.0 ppm.

<sup>31</sup>P NMR: 25.65 ppm.

#### Catalytic experiments

All reactions were performed using screw-cap tubes in a multireactor system. In a typical experiment: aniline (7a, 0.5 mmol,

49 µL) and ethyl diazoacetate (8, 0.5 mmol, 53 µL) were added to a reactor tube containing the complex cis-[Re(p-NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)-Cl<sub>2</sub>(py-2-COO)(PPh<sub>3</sub>)] (3, 2.5 mg, 0.0034 mmol, 0.68 mol%) without a 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-(Cl,Cl)-[Re(p-NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)-Cl<sub>2</sub>(py-2-COO)(PPh<sub>3</sub>)] and cis-(Cl,Cl)-[Re(p-NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)Cl<sub>2</sub>(py-2-COO)(PPh<sub>3</sub>)] were optimized without any symmetry restrictions in singlet ground-states with the DFT method using the GAUSSIAN-03 program package.22 The calculations were performed using three DFT methods (B3LYP, BP86, and PBE1PBE) in combination with several basis sets.<sup>23</sup> The basis sets tested in this work are described in Table 2. The optimized geometries of trans-(Cl,Cl)-[Re(p-NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)Cl<sub>2</sub>(py-2-COO)(PPh<sub>3</sub>)] and cis-(Cl,Cl)-[Re(p-NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)Cl<sub>2</sub>(py-2-COO)-(PPh<sub>3</sub>)] were verified by performing frequency calculations. The absence of an imaginary frequency ensures that the optimized geometries correspond to true energy minima. All the subsequent calculations were performed based on optimized geometries using the PBE1PBE method in combination with the basis sets presented 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).<sup>25</sup>

# Acknowledgements

The GAUSSIAN-03 calculations were carried out in the Wrocław Centre for Networking and Supercomputing, WCSS, Wrocław, Poland, http://www.wcss.wroc.pl, under calculational grant no. 18. This work was generously supported by the Spanish Ministerio de Economía y Competitividad (MINECO; CTQ2007-65218 and Consolider Ingenio 2010-CSD2007-00006), the Generalitat Valenciana (GV; PROMETEO/2009/039), and Fondo Europeo de Desarrollo Regional (FEDER). Y. M. acknowledges the Instituto de Síntesis Orgánica (ISO) of the Universidad de Alicante for a grant.

# References

- (a) S. S. Jurisson and J. D. Lydon, *Chem. Rev.*, 1999, 99, 2205–2218; (b) S. Liu and D. S. Edwards, *Chem. Rev.*, 1999, 99, 2235–2268; (c) E. S. Mull, V. J. Sattigeri, A. L. Rodriguez and J. A. Katzenellenbogen, *Bioorg. Med. Chem.*, 2002, 10, 1381–1398; (d) P. Blower, *Dalton Trans.*, 2006, 1705–1711; (e) U. Abram and R. Alberto, *J. Braz. Chem. Soc.*, 2006, 17, 1486–1500; (f) B. Coutinho, D. Dawson, J. R. Dilworth, J. R. Miller, M. Rosser, C. M. Archer and J. D. Kelly, in: *Technetium and Rhenium in Chemistry and Nuclear Medicine*, ed. M. Nicolini, G. Bandoli, U. Mazzi and S. G. Editoriali, Padova, 1995, vol. 3.
- 2 (a) R. Hua and J.-L. Jiang, *Curr. Org. Synth.*, 2007, 4, 151–174; (b) Y. Kuninobu and K. Takai, *Chem. Rev.*, 2011, **111**, 1938–1953.
- 3 (a) J. J. Kennedy-Smith, K. A. Nolin, H. P. Gunterman and F. D. Toste, *J. Am. Chem. Soc.*, 2003, **125**, 4056–4057;
  (b) K. A. Nolin, J. R. Krumper, M. D. Puth, R. G. Bergman and F. D. Toste, *J. Am. Chem. Soc.*, 2007, **129**, 14684–14696;
  (c) S. C. A. Sousa, I. Cabrita and A. C. Fernandes, *Chem. Soc. Rev.*, 2012, **41**, 5641–5653.
- 4 Z. Zhu and J. H. Espenson, J. Am. Chem. Soc., 1996, 118, 9901–9907.
- 5 (a) B. Machura, R. Kruszynski and J. Kusz, Polyhedron, 2008, 27, 1679–1689; (b) B. Machura and J. Kusz, Polyhedron, 2008, 27, 366–374; (c) B. Machura, A. Świtlicka, M. Wolff, J. Kusz and R. Kruszynski, Polyhedron, 2009, 28, 2949–2964; (d) B. Machura, M. Wolff, J. Palion and R. Kruszynski, Inorg. Chem. Commun., 2011, 14, 1358–1361; (e) B. Machura, M. Wolff and J. Kusz, Polyhedron, 2010, 29, 1619–1629; (f) B. Machura, M. Wolff, D. Tabak, J. A. Schachner and N. C. Mösch-Zanetti, Eur. J. Inorg. Chem., 2012, 3764–3773.
- 6 B. Machura, M. Wolff, A. Świtlicka and I. Gryca, *Polyhedron*, 2010, **29**, 2381–2392.
- 7 (a) A. M. Kirillov, M. Haukka and A. J. L. Pombeiro, *Inorg. Chim. Acta*, 2006, 359, 4421–4426; (b) S. Michalik, J. G. Malecki, R. Kruszynski, V. Kozik, J. Kusz and M. Krompiec, *J. Coord. Chem.*, 2011, 64, 2202–2213.
- 8 F. H. Allen, Acta Crystallogr., Sect. B: Struct. Sci., 2002, 58, 380-388.
- 9 A. Sachse, N. C. Mösch-Zanetti, G. Lyashenko, J. W. Wielandt, K. Most, J. Magull, F. Dall'Antonia, A. Pal and R. Herbst-Irmer, *Inorg. Chem.*, 2007, 46, 7129–7135.
- A. M. Kirillov, M. Haukka, M. V. Kirillova and
   A. J. L. Pombeiro, *Adv. Synth. Catal.*, 2005, 347, 1435–1446.
- (a) R. Rossi, A. Marchi, A. Duatti, L. Magon, U. Casellato, R. Graziani and G. Polizzotti, *Inorg. Chim. Acta*, 1984, 90, 121–131; (b) V. M. Bereau, S. I. Khan and M. M. Abu-Omar, *Inorg. Chem.*, 2001, 40, 6767–6773; (c) B. Machura, I. Gryca and M. Wolff, *Polyhedron*, 2012, 31, 128–135; (d) B. Machura, M. Wolff and I. Gryca, *Polyhedron*, 2011, 30, 142–153; (e) B. Machura, M. Wolff and I. Gryca, *Inorg. Chim. Acta*, 2011, 370, 7–17.

- 12 G. B. Deacon and R. J. Phillips, *Coord. Chem. Rev.*, 1980, 33, 227–250.
- 13 A. M. Kirillov, M. Haukka and A. J. L. Pombeiro, *Inorg. Chim. Acta*, 2006, **359**, 4421–4426.
- 14 S. R. Flechter and A. C. Skapski, J. Chem. Soc., Dalton Trans., 1972, 1073-1078.
- 15 M. Turki, C. Daniel and S. Záliš, J. Am. Chem. Soc., 2001, 123, 11431–11440.
- 16 M. L. Kuznetsov, E. A. Klestova-Nadeeva and A. I. Dement'ev, J. Mol. Struct. (THEOCHEM), 2004, 671, 229–237.
- 17 M. P. Doyle, M. A. McKervey and T. Ye, Modern Catalytic Methods for Organic Synthesis with Diazo Compounds: from Cyclopropanes to Ylides, John Wiley & Sons, New York, 1998, ch. 8.
- 18 H. Braband, T. I. Kückmann and U. Abram, J. Organomet. Chem., 2005, 690, 5421–5429.
- 19 J. Chatt, J. D. Garforth, N. P. Johnson and G. A. Rowe, *J. Chem. Soc.*, 1964, 1012–1020.
- 20 Oxford Diffraction. CrysAlis PRO. Oxford Diffraction Ltd, Yarnton, England, 2011.
- 21 (a) G. M. Sheldrick, SHELXS-97. Program for Crystal Structure Resolution, Univ. of Göttingen, Göttingen, Germany, 1997;
  (b) G. M. Sheldrick, SHELXL-97. Program for Crystal Structures Analysis, Univ. of Göttingen, Göttingen, Germany, 1997.
- 22 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone,

B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Hevd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, Revision A.1, Gaussian, Inc., Wallingford CT, 2009.

- 23 (a) J. Gancheff, C. Kremer, E. Kremer and O. N. Ventura, *J. Mol. Struct. (THEOCHEM)*, 2002, 580, 107–116;
  (b) J. S. Gancheff, P. A. Denis and F. E. Hahn, *J. Mol. Struct. (THEOCHEM)*, 2012, 941, 1–9.
- 24 (a) E. D. Glendening, A. E. Reed, J. E. Carpenter and F. Weinhold, *NBO Version 3.1*; (b) E. Reed, L. A. Curtiss and F. Weinhold, *Chem. Rev.*, 1988, 88, 899–926.
- 25 M. E. Casida, in *Theoretical and Computational Chemistry*, ed. J. M. Seminario, Elsevier, Amsterdam, 1996, ch. 4.