

Single-Pot Ethane Carboxylation Catalyzed by New Oxorhenium(V) Complexes with N,O Ligands

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Abstract: The oxorhenium(V) chelates [ReOCl₃(N,O-L)(PPh₃)₂] [N,O-L = (OCH₂CH₂)N(CH₂CH₂OH)-(CH₂COO) (2), (OCH₂CH₂)N(CH₂COO)(CH₂-COOCH₃) (3)] and [ReOCl₃(N,O-L)(PPh₃)₂] [N,O-L = C₅H₄N(COO-2) (4) C₅H₃N(COOCH₃-2)(COO-6) (5)] have been prepared by reaction of [ReOCl₃(PPh₃)₂] (1), in refluxing methanol, with *N,N*-bis(2-hydroxyethyl)glycine [bicine; N(CH₂CH₂OH)₂(CH₂COOH)], *N*-(2-hydroxyethyl)iminodiacetic acid [N(CH₂CH₂OH)(CH₂COOH)₂], picolinic acid [NC₅H₄(COOH-2)] or 2,6-pyridinedicarboxylic acid [NC₅H₃(COOH-2,6)], respectively, with ligand esterification in the cases of 3 and 5. All these complexes have been characterized by IR and multinuclear NMR spectroscopy, FAB⁺-MS, elemental and X-ray diffraction structural analyses. They act as catalysts, in a single-pot process, for the carboxylation of ethane by CO, in the presence of potassium peroxodisulfate K₂S₂O₈, in tri-

fluoroacetic acid (TFA), to give propionic and acetic acids, in a remarkable yield (up to ca. 30%) and under relatively mild conditions, with some advantages over the industrial processes. The picolinate complex 4 provides the most active catalyst and the carboxylation also occurs, although much less efficiently, by the TFA solvent in the absence of CO. The selectivity can be controlled by the ethane and CO pressures, propionic acid being the dominant product for pressures about ca. 7 and 4 atm, respectively (catalyst 4), whereas lower pressures lead mainly to acetic acid in lower yields. These reactions constitute an unprecedented use of Re complexes as catalysts in alkane functionalization.

Keywords: alkanes; carboxylation; C–H activation; homogeneous catalysis; N,O ligands; rhenium

Introduction

The oxo chemistry of rhenium is attracting much interest, in particular due to the discovery that methyltrioxorhenium [(Me)ReO₃] and its derivatives are among the most versatile oxidation catalysts known to date.^[1,2] Nevertheless, the application of *inorganic* coordination compounds of rhenium in catalysis still remains an underdeveloped field, namely in the functionalization of unsaturated hydrocarbons and their derivatives,^[3] and is almost unexplored with respect to alkanes, except for (i) some alkane dehydrogenation reactions, commonly in rather low yields, catalyzed by rhenium polyhydrides in the presence of a hydrogen acceptor, driven by continuous removal of H₂ or under irradiation,^[4] and (ii) for a few peroxidative oxidations of cycloalkanes catalyzed, also in low yields, by rhenium benzoylhydrazido and -diazenido complexes.^[5] Alkanes (namely the gaseous ones, methane, ethane and propane) are the most prevalent and relatively cheap natural sources of organic matter and their effective utilization by conversion to

more valuable oxidized products is a field of currently growing interest with industrial relevance.^[6]

Recently, we have found that some rhenium^[5] and vanadium^[7,8] compounds containing amino alcohol and amino carboxylate ligands catalyze the peroxidative hydroxylation, oxygenation and halogenation of cycloalkanes,^[5,7] and the conversion of *methane* into acetic acid.^[8] The latter reaction has also been noticeably explored by others^[9] following various routes and with different types of metal catalysts, but not with Re. Of particular significance to our work is the metal catalyst/potassium peroxodisulfate/trifluoroacetic acid system pioneered by Fujiwara et al.^[9e–k,m] This active research contrasts with the case of carboxylation of *ethane* to propionic acid^[10–14] which has been investigated rather scantily (usually limited to single experiments) in spite of (i) the wide application of this acid for the preparation of various derivatives (broadly applied^[15] as food and feed preservatives, herbicides, therapeutic agents, perfumes, inhibitors, in liquid crystal mixtures, etc.) and (ii) the difficulties to its industrial manufacture,^[15a] usu-

ally requiring drastic conditions (high temperatures and pressures), more than one synthetic stage and/or leading to a product mixture that requires a further complex work-up. A main objective of the current study was thus to search for Re complexes that could catalyze the functionalization of ethane into carboxylic acids, i.e., propionic and acetic acids, if possible in a process that could overcome some of these limitations.

It is also known that iron(II and III) complexes with picolinic acid are components in efficient Gif systems^[16] which are active for the functionalization of liquid alkanes. In the past two decades Gif chemistry was widely explored,^[17] but Re catalysts were not described. Moreover, such systems have not yet been applied to gaseous alkanes, except in a single case involving the oxidation of *n*-butane and propane.^[18] Thus, of particular interest to our study would be the use of picolinate and related ligands in our Re/ethane systems, although they are quite different from the Gif ones.

As starting material we have selected the rhenium(V) compound $[\text{ReOCl}_3(\text{PPh}_3)_2]$ (**1**) that is a common precursor for a variety of oxorhenium complexes (some of which are of pharmaceutical significance),^[20] namely with polydentate N,O-donor ligands.^[21–23] However, since its use with amino alcohol or amino carboxylate N,O ligands is still scarce,^[24] another aim of this work was to extend its application to this type of ligands, namely picolinic acid $[\text{NC}_5\text{H}_4(\text{COOH}-2)]$, 2,6-pyridinedicarboxylic acid $[\text{NC}_5\text{H}_3(\text{COOH}-2,6)_2]$, the glycine derivative $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2(\text{CH}_2\text{COOH})$ and *N*-(2-hydroxyethyl)iminodiacetic acid $[\text{N}(\text{CH}_2\text{CH}_2\text{OH})(\text{CH}_2\text{COOH})_2]$.

Hence, in the current study we have prepared new oxorhenium(V) complexes with these chelating N,O ligands and found that they can exhibit a remarkable catalytic activity for the conversion of ethane, under relatively mild conditions, to a mixture of propionic and acetic acids (overall yield up to 30%, based on the alkane), in a single-pot process with various advantages over the industrial ones. This constitutes a very rare example of the application of *inorganic* rhenium complexes as catalysts in the field of alkane functionalization and the most active Re catalytic system (among either the inorganic or the organometallic species), so far reported in this field.

Results and Discussion

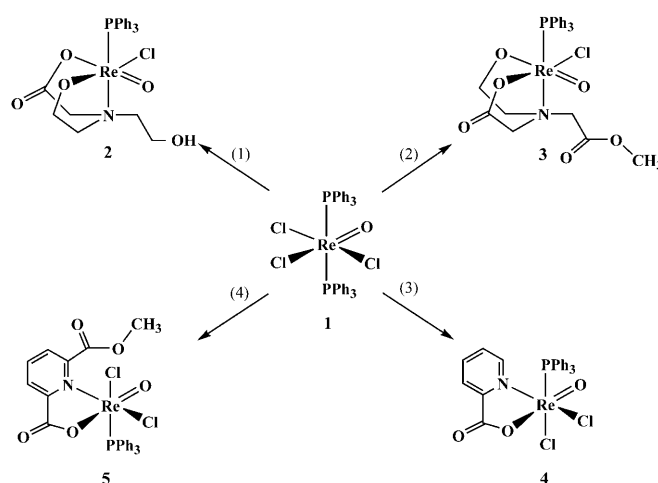
Synthesis and Spectroscopic Characterization

The reactions of $[\text{ReOCl}_3(\text{PPh}_3)_2]$ (**1**) with the aliphatic or aromatic N,O-species $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2(\text{CH}_2\text{COOH})$ (bicine), $\text{N}(\text{CH}_2\text{CH}_2\text{OH})(\text{CH}_2\text{COOH})_2$ [*N*-(2-hydroxyethyl)iminodiacetic acid], $\text{NC}_5\text{H}_4(\text{COOH}-2)$ (picolinic acid) or $\text{NC}_5\text{H}_3(\text{COOH}-2,6)_2$ (2,6-pyridinedicarboxylic

acid), in refluxing methanol, led to the formation of the neutral oxorhenium(V) complexes $[\text{ReOCl}\{(\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{OH})(\text{CH}_2\text{COO}))(\text{PPh}_3)\}]$ (**2**), $[\text{ReOCl}\{(\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{COO})(\text{CH}_2\text{COOCH}_3))(\text{PPh}_3)\}]$ (**3**), $[\text{ReOCl}_2\{\text{C}_5\text{H}_4\text{N}(\text{COO}-2)\}(\text{PPh}_3)]$ (**4**) or $[\text{ReOCl}_2\{\text{C}_5\text{H}_3\text{N}(\text{COOCH}_3-2)(\text{COO}-6)\}(\text{PPh}_3)]$ (**5**), respectively, in 87–42% isolated yields, as shown in Scheme 1 (reactions a–d). All these complexes are stable in the solid state, **4** and **5** are also stable in Me_2CO , CH_2Cl_2 , MeCN or CHCl_3 solution, whereas **2** and **3** decompose slowly within a few days in these solvents. All compounds were characterized by IR, ^1H , $^{31}\text{P}\{^1\text{H}\}$ and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy, FAB⁺-MS, elemental and single crystal X-ray diffraction structural analyses.

In the formation of the purple complexes **2** and **3** (reactions a and b, Scheme 1), bicine and *N*-(2-hydroxyethyl)iminodiacetic acid, respectively, provided (upon deprotonation of one carboxylic acid group and one hydroxyethyl arm) dianionic tridentate N,O,O ligands which replace one triphenylphosphine and two chlorides. In reactions c and d (Scheme 1), picolinic acid and 2,6-pyridinedicarboxylic acid, respectively, formed bidentate monoanionic N,O ligands (upon deprotonation of one carboxylic acid group) which replace one triphenylphosphine and one chloride in **1** to afford the corresponding reddish purple complex **4** and the greenish grey compound **5**, as microcrystalline materials.

In complexes **2**, **3** and **5** the N,O,O or N,O ligand exhibits one free O-arm. In **2** this is a free hydroxyethyl group, in accord with the detection, in the IR spectrum, of a strong and broad $\nu(\text{OH})$ band at 3364 cm^{-1} , whereas in **3** and **5** it is a methyl acetate moiety formed by esterification of one carboxylic acid by MeOH, presumably under the influence of the metal centre since the ester is not formed in blank experiments with *N*-(2-hydroxyethyl)iminodiacetic or 2,6-pyridinedicarboxylic acid and methanol, upon refluxing for 8 h in the absence of



Scheme 1. (a) $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2(\text{CH}_2\text{COOH})$, (b) $\text{N}(\text{CH}_2\text{CH}_2\text{OH})(\text{CH}_2\text{COOH})_2$, (c) $\text{NC}_5\text{H}_4(\text{COOH}-2)$, (d) $\text{NC}_5\text{H}_3(\text{COOH}-2,6)_2$.

complex **1**. The methyl ester group was confirmed by the IR spectra of **3** and **5** which exhibit strong bands assigned to $\nu_{\text{as}}(\text{COOMe})$ [1744 (**3**) or 1743 (**5**) cm^{-1}] and $\nu_{\text{s}}(\text{COOMe})$ [1341 (**3**) or 1334 (**5**) cm^{-1}].^[25] Besides, the corresponding methyl signals were detected in the ^1H [$\delta=3.84$ (**3**) or 3.66 (**5**)] and $^{13}\text{C}\{^1\text{H}\}$ [$\delta=52.38$ (**3**) or 53.39 (**5**)] NMR spectra. Despite the fact that related complexes with *N*-(2-hydroxyethyl)iminodiacetate and 2,6-pyridinedicarboxylate were previously synthesized for different metals, the ester derivatives of these ligands in compounds **3** and **5** [i.e., *N*-(2-oxyethyl)(2-methoxycarbonylmethyl)iminoacetate [$^-\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{COO}^-)\text{CH}_2\text{COOCH}_3$] and 2-methoxycarbonyl-6-pyridinecarboxylate [$\text{C}_5\text{H}_3\text{N}(\text{COOCH}_3-2)(\text{COO}^- -6)$], respectively] constitute, to the best of our knowledge, the first such examples in metal complexes.

The IR spectra of all complexes exhibit characteristic strong intensity $\nu(\text{Re}=\text{O})$ bands at 957 (**2**, **3**), 988 (**4**) and 1001 (**5**) cm^{-1} , values in good agreement with those reported for other oxorhenium compounds.^[22d,22e,26] Additional bands in the regions 1707–1650 and 1437–1434 cm^{-1} are assigned to the $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$, respectively.^[25]

The molecular ions were clearly observed with the expected isotopic patterns in the FAB^+ -MS of all compounds, except **3** for which the heaviest fragment was ($\text{M}^+ - \text{Cl}$). Other peaks correspond to the stepwise fragmentations by loss of Cl, PPh_3 and N,O ligand fragments. The $^{31}\text{P}\{^1\text{H}\}$ spectra are diagnostic of triphenylphos-

phine coordination,^[27] the corresponding signal is slightly shifted downfield from $\delta = -5.47$ ppm in the uncoordinated phosphine to 2.67 (**2**) and 3.75 (**3**), and upfield to -10.80 (**4**) and -11.83 ppm (**5**). The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra show resonances at the usual chemical shifts for the coordinated PPh_3 and N,O,O or N,O ligands.^[22a,22e,28] Elemental analyses are also consistent with the proposed formulations which are authenticated by single crystal X-ray diffraction studies, as indicated below.

X-Ray Crystal Structures

The crystallographic data are summarized in Table 1 and selected bond lengths and angles in Table 2. The molecular structures of complexes **2–5** are shown in Figures 1–4. All compounds **2–5** present a distorted octahedral coordination geometry about rhenium, consisting of the N,O,O or N,O ligand, PPh_3 , the oxo and one or two chloride ligands.

In complex **2** (Fig. 1) bicine is doubly deprotonated and ligates the rhenium through the ethoxy oxygen O1 *trans* to chloride, the carboxylate oxygen O2 *trans* to the oxo group and the amino nitrogen N1 which is *trans* to the triphenylphosphine ligand. The binding of the bicine ligand involves the chelate rings $\text{Re}-\text{N1}-\text{C2}-\text{C3}-\text{O1}$ and $\text{Re}-\text{N1}-\text{C4}-\text{C3}-\text{O2}$ with bite angles of $\text{N1}-\text{Re}-\text{O1}$ $82.4(3)^\circ$ and $\text{N1}-\text{Re}-\text{O2}$

Table 1. Crystal data and structure refinement details for compounds **2–5**.

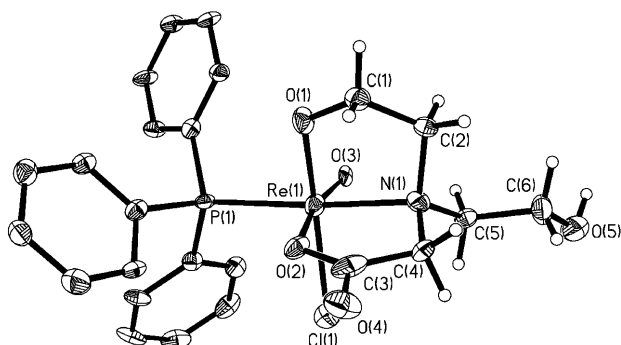
	2	3	4	5
empirical formula	$\text{C}_{24}\text{H}_{26}\text{ClNO}_5\text{Pre}$	$\text{C}_{25}\text{H}_{26}\text{ClNO}_6\text{Pre}$	$\text{C}_{24}\text{H}_{19}\text{Cl}_2\text{NO}_3\text{Pre}$	$\text{C}_{26}\text{H}_{21}\text{Cl}_2\text{NO}_5\text{Pre}$
Fw	661.08	689.09	657.47	715.51
temp (K)	100(2)	100(2)	293(2)	100(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073
cryst. syst.	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	C c	$P2_1/c$
<i>a</i> (Å)	10.4728(4)	15.6260(15)	7.5697(6)	9.6672(14)
<i>b</i> (Å)	9.1751(4)	10.6661(13)	39.306(5)	32.4691(15)
<i>c</i> (Å)	24.8023(7)	15.9049(12)	7.8335(8)	8.5137(10)
α (deg)	90	90	90	90
β (deg)	98.801(2)	111.500(8)	96.13(3)	111.162(10)
γ (deg)	90	90	90	90
<i>V</i> (Å ³)	2355.17(15)	2466.4(4)	2317.4(4)	2492.1(5)
<i>Z</i>	4	4	4	4
ρ_{calc} (Mg/m ³)	1.864	1.856	1.884	1.907
$\mu(\text{Mo K}\alpha)$ (mm ⁻¹)	5.378	5.142	5.570	5.194
no. of collected reflns	23401	21887	9039	12653
no. of unique reflns	4217	5624	4183	5660
R_{int}	0.0602	0.0443	0.0250	0.0256
final $R1^{[a]}$, $wR2^{[b]}$ ($I \geq 2\sigma$)	0.0695, 0.1407	0.0281, 0.0497	0.0189, 0.0457	0.0249, 0.0520
$R1$, $wR2$ (all data)	0.0824, 0.1457	0.0487, 0.0549	0.0205, 0.0463	0.0338, 0.0544
GOF on F^2	1.306	1.088	0.897	1.106
largest diff. peak and hole, e Å ⁻³	3.473, -2.256	1.933, -1.349	0.770, -1.763	0.849, -1.739

^[a] $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.

^[b] $wR2 = [\sum (w(F_o^2 - F_c^2))^2 / \sum (w(F_o^2)^2)]^{1/2}$.

Table 2. Selected bond lengths (Å) and angles (deg) for compounds **2–5**.

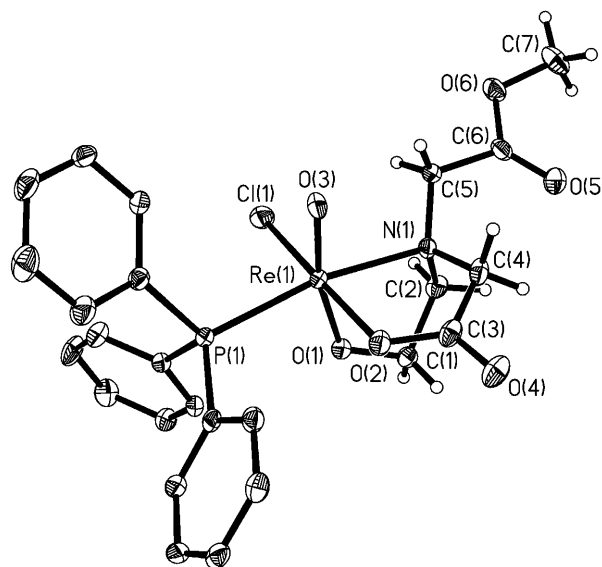
	2	3	4	5
Re–N(1)	2.235(10)	2.259(3)	2.138(4)	2.186(3)
Re–O(1)	1.943(9)	1.908(3)	2.067(3)	2.037(2)
Re–O(2)	2.052(9)	2.058(3)		
Re–O(3)	1.860(9)	1.729(3)	1.663(3)	1.672(2)
Re–Cl(1)	2.361(3)	2.3831(11)	2.3294(10)	2.3227(9)
Re–Cl(2)			2.3650(14)	2.3645(9)
Re–P(1)	2.441(3)	2.4324(10)	2.4551(11)	2.4685(9)
O(1)–Re–O(3)	101.5(4)	166.85(12)	158.60(15)	163.41(10)
O(1)–Re–Cl(1)	163.8(3)	89.65(9)	96.57(9)	93.81(7)
O(2)–Re–O(3)	168.8(3)	92.25(13)		
O(2)–Re–Cl(1)	82.3(2)	172.78(8)		
O(3)–Re–Cl(1)	93.9(3)	93.32(10)	102.36(12)	101.35(8)
N(1)–Re–O(3)	91.8(3)	89.27(12)	87.42(17)	89.93(10)
N(1)–Re–O(1)	82.4(3)	77.69(11)	74.65(15)	75.16(10)
N(1)–Re–O(2)	77.9(3)	79.87(11)		
N(1)–Re–P(1)	174.3(3)	169.06(8)	96.94(11)	90.29(7)
N(1)–Re–Cl(1)	92.0(3)	95.61(9)	169.29(13)	168.63(7)

**Figure 1.** An ORTEP-3 representation of **2**. Ph hydrogen atoms have been omitted for clarity.

79.87(11)°. The Re–N1 bond length, 2.235(10) Å, is significantly longer than the Re–O1 1.943(9) and Re–O2 2.052(9) Å ones (Table 2), as commonly observed for N,O,O or N,O donor ligands in oxorhenium complexes.^[22d,22e] The Re–O3 distance of 1.860(9) Å is much longer than the normal Re–O_{oxo} bond length (*ca.* 1.67–1.70 Å)^[29] in six-coordinated monooxorhenium complexes. This could point to a considerable *trans* influence of the carboxylate ligand, but is not observed for complexes **4** and **5**. Alternatively, it could be accounted for by considering the possible contamination of **2** by its isomer with the oxo-ligand *trans* to a ligand ethoxy arm (as in **3**) and thus the chloro ligand (with a much longer coordination bond length) *trans* to the carboxylate arm. The O1–Re–O3 angle of 101.5(4)°, *i.e.*, between the Re=O and the adjacent Re–O bonds is remarkably larger than 90°. Other bond lengths and angles do not differ significantly from the expected values found for oxorhenium compounds containing N, O, P and Cl donor atoms.^[22b–22g]

The coordination geometry around the rhenium centre in **3** (Fig. 2) is similar to that of **2** with the exception that the chelated ethoxy arm is *trans* to the oxo ligand instead of the carboxylate group. Most of the bonding parameters in **3** (Table 2) are comparable with those of complex **2** apart from the Re–O3 bond, 1.729(3) Å, which is significantly shorter and has a length that is in the normal range for such a type of bond.^[29]

The molecular structure of **4** (Fig. 3) exhibits a triphenylphosphine ligand *trans* to the chloride Cl2, and a picolinate, chloride Cl1 and oxo atom in the equatorial sites. In the picolinate NC₅H₄COO[–] ligand, the nitrogen N1 is *trans* to the chloride Cl1 and the carboxylate oxygen O1 *trans* to the oxo atom, forming an

**Figure 2.** An ORTEP-3 representation of **3**. Ph hydrogen atoms have been omitted for clarity.

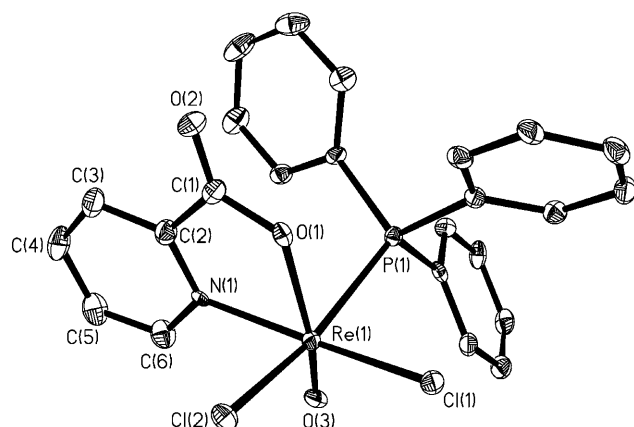


Figure 3. An ORTEP-3 representation of **4**. Ph hydrogen atoms have been omitted for clarity.

Re–N1–C2–C1–O1 ring with an N1–Re–O1 bite angle of $74.65(15)^\circ$ which is reduced significantly from the expected octahedral value of 90° . The Re–N1 and Re–O3 distances [2.138(4) and 1.663(3) Å, respectively] are shorter than the corresponding ones in **2** and **3** (Table 2), whereas the Re–O1 bond length of 2.067(3) Å is longer, and this can indicate a stronger interaction of the metal with the oxo ligand. Most of the bond distances of complex **4** are comparable to those of related oxo complexes with picolinate or 3-hydroxypicolinate such as $[\text{ReO}(\text{Me})(\text{NC}_5\text{H}_4\text{COO})_2]$, $[\text{ReOI}_2[\text{NC}_5\text{H}_3(\text{OH}-3)\text{COO}](\text{PPh}_3)]$ and $[\text{ReOCl}_3[\text{NC}_5\text{H}_3(\text{OH}-3)\text{COO}]]$.^[22j,30]

In **5** the coordination geometry around the rhenium centre (Fig. 4) and the metal-ligand distances are analogous to those of **4**, although with swapped positions of

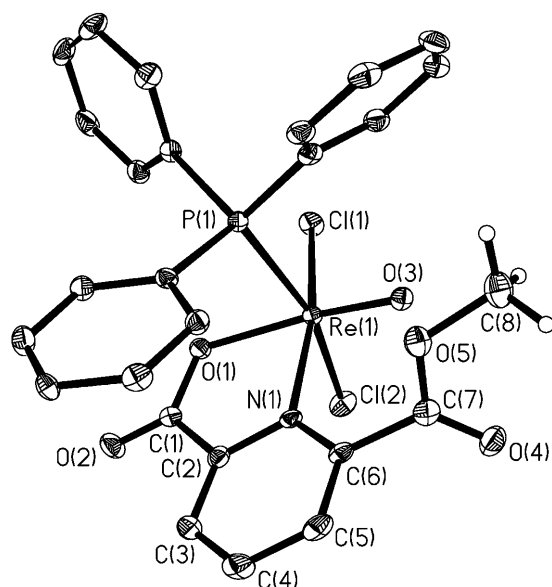


Figure 4. An ORTEP-3 representation of **5**. Ph hydrogen atoms have been omitted for clarity.

the PPh_3 and Cl_2 ligands. In both dichloro complexes, the Re–Cl1 bond [2.3294(10) Å for **4**; 2.3227(9) Å for **5**] *trans* to N1 is slightly shorter than the Re–Cl2 bond [2.3650(14) Å for **4**; 2.3645(9) Å for **5**] *trans* to the triphenylphosphine. Most of the binding parameters of the N,O ligand in **5** compare favorably with those found in $[\text{ReBr}[\text{NC}_5\text{H}_3(\text{COOMe}-6)\text{COOEt}](\text{CO})_3]$.^[31]

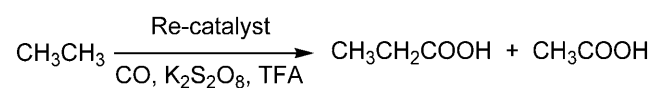
The Re–P1 distances in all compounds **2–5** (2.43–2.47 Å) (Table 2) are in accordance with those reported^[22h,24d,26b,28d,32] for other oxorhenium triphenylphosphine complexes.

Catalytic Activity of Rhenium Complexes towards Ethane Carboxylation

All the rhenium complexes **1–5**, in the presence of $\text{K}_2\text{S}_2\text{O}_8$ and in trifluoroacetic acid (TFA) at 80°C , exhibit catalytic activity for the carboxylation of ethane with carbon monoxide to give propionic acid (Scheme 2 and Table 3). Acetic acid is also formed as a result of the competitive Re-catalyzed partial oxidation of ethane by the peroxodisulfate. Complex **4**, with a picolinate ligand, provides the most active catalyst (overall yields and TONs up to *ca.* 30% and 45, respectively, entry 10), being followed by compounds **3** and **2**. The other complexes, **1** and **5**, are much less active, catalyzing mainly the oxidation of ethane to acetic acid. Complexes **3** and **4** also exhibit better selectivity towards the formation of propionic acid, the propionic-to-acetic acid molar ratios reaching the value of *ca.* 5:1.

Since it became apparent that the complex **4** is the most active and selective catalyst for the formation of propionic acid, the effects of CO and C_2H_6 pressure on the yield of products and on the TON were investigated for that catalyst, for the purpose of optimization of the conditions. The amount of carbon monoxide has a relevant effect on the yield of propionic acid (Fig. 5; entries 6–11, Table 3) which gradually increases with the CO pressure up to 30 atm, for a constant pressure (10 atm) of C_2H_6 . However, further enhancement of *p*CO markedly decreases that yield, conceivably due to the deactivation of the catalyst as a result of formation of carbonyl complexes. Hence, higher CO pressures should be avoided. The TON and the selectivity (propionic-to-acetic acid molar ratios) follow similar dependences on the CO pressure.

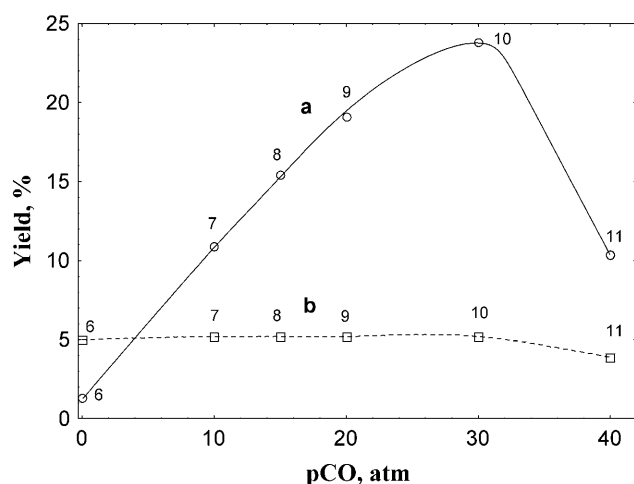
In the absence of added CO, an appreciable amount of propionic acid is still formed (1.3% yield, entry 6), the TFA behaving as the carbonylating agent of ethane. Hence, the previously recognized^[8,9d] ability of TFA to



Scheme 2.

Table 3. Catalytic activity of complexes **1** – **5** towards the carboxylation of ethane.

Entry	Catalyst	Amount of catalyst [mmol]	$p\text{C}_2\text{H}_6$ [atm]	$p\text{CO}$ [atm]	Yield ^[a] [%]			TON ^[c]	Molar ratio propionic/acetic acid
					Propionic acid	Acetic acid	Total ^[b]		
1	1	0.01	10	15	0.2	1.9	2.1	6.4	0.1:1
2	2	0.01	10	15	2.0	3.5	5.5	17.0	0.6:1
3	3	0.01	10	15	4.5	2.6	7.1	22.0	1.7:1
4	4	0.01	10	15	7.7	4.3	12.0	37.0	1.8:1
5	5	0.01	10	15	0.0	1.5	1.5	2.3	–
6	4	0.02	10	0	1.3	5.0	6.3	9.5	0.3:1
7	4	0.02	10	10	10.9	5.2	16.1	24.6	2.1:1
8	4	0.02	10	15	15.4	5.2	20.6	31.5	3.0:1
9	4	0.02	10	20	19.1	5.2	24.3	37.2	3.7:1
10	4	0.02	10	30	23.8	5.2	29.0	44.5	4.6:1
11	4	0.02	10	40	10.4	3.9	14.3	22.0	2.7:1
12	4	0.02	5	30	2.5	5.6	8.1	6.3	0.4:1
13	4	0.02	15	30	0.5	1.1	1.6	3.7	0.5:1
14 ^[d]	4	0.02	10	30	23.6	5.4	29.0	44.5	4.4:1
15	1	0.02	10	20	4.2	2.0	6.2	9.5	2.1:1
16 ^[d]	1	0.02	10	20	4.7	2.2	6.9	10.5	2.1:1
17 ^[e]	4	0.02	10	30	–	0.3	0.3	0.5	–
18 ^[f]	4	0.02	10	30	–	0.8	0.8	1.2	–
19 ^[g]	4	0.02	10	30	–	1.0	1.0	1.5	–
20 ^[h]	4	0.02	10	30	0.2	–	0.2	0.3	–

^[a] Moles of product/100 moles of ethane.^[b] Propionic acid + acetic acid.^[c] Moles of product (propionic acid + acetic acid)/mol of catalyst.^[d] 0.2 mmol of picolinic acid were added to the reaction mixture.^[e] In the presence of CBrCl₃ (1:1, relatively to ethane).^[f] In the presence of 2,2,6,6-tetramethylpiperidine-1-oxyl (0.5:1, relatively to ethane).^[g] In the presence of Ph₂NH (1:1, relatively to ethane).^[h] In the presence of 2,6-di-*tert*-butyl-4-methylphenol (1:1 or 0.5:1, relatively to ethane).**Figure 5.** Effect of the CO pressure on the yield of propionic (a) and acetic (b) acid in the ethane carboxylation catalyzed by complex **4** ($p\text{C}_2\text{H}_6 = 10$ atm). Point numbers are those of the Table 3 entries.

carboxylate methane, when using some vanadium catalysts, has now been extended to ethane in the presence of

Re catalysts. The yield of acetic acid practically does not depend on the CO pressure from 0 up to 30 atm, indicating that CO is not involved in this peroxidative oxidation process. Moreover, since the propionic acid yield decreases with a decrease of $p\text{CO}$ (below *ca.* 30 atm), the selectivity towards this acid also decreases and, for pressures below *ca.* 4 atm, acetic acid becomes the main product.

The pressure of ethane has also an important effect on the yields of the products (Fig. 6, for a constant pressure, 30 atm, of CO). Thus, the yield of propionic acid increases upon increasing the C_2H_6 pressure to 10 atm, beyond which a decrease occurs. The yield of acetic acid is less dependent on the C_2H_6 pressure and inversion of the selectivity occurs for $p\text{C}_2\text{H}_6$ below *ca.* 7 atm when that acid becomes the dominant product. Therefore, the selectivity can be controlled by both $p\text{C}_2\text{H}_6$ and (see above) $p\text{CO}$: pressures above *ca.* 7 and *ca.* 4 atm, respectively, lead to the predominance of propionic acid, relatively to acetic acid, and, for the best yield of propionic acid and the best selectivity, the optimum $p\text{C}_2\text{H}_6$ and $p\text{CO}$ are 10 and 30 atm, respectively. In contrast, the formation of acetic acid, which does not involve carbonylation,

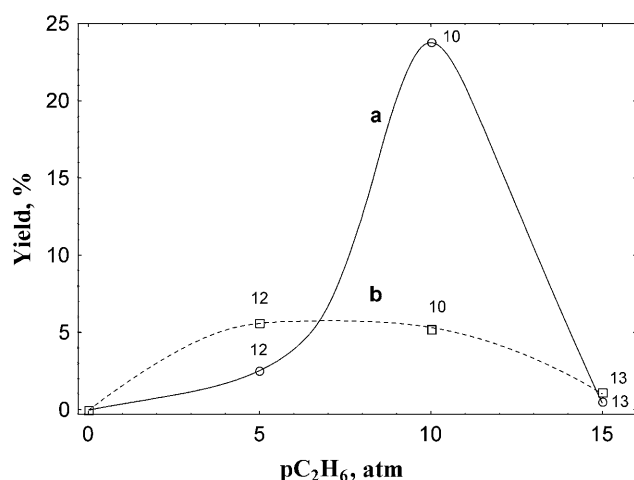


Figure 6. Effect of the C_2H_6 pressure on the yield of propionic (a) and acetic (b) acid in the ethane carboxylation catalyzed by complex **4** ($p\text{CO} = 30$ atm). Point numbers are those of the Table 3 entries.

predominates over that of propionic acid for $p\text{C}_2\text{H}_6$ and $p\text{CO}$ lower than *ca.* 7 and 4 atm, respectively.

Since complex **4**, with a picolinate ligand, is the most active catalyst and picolinic acid (either incorporated in the catalyst^[16] or added as an additive to the reaction mixture)^[17,33] is known to enhance strongly the rate of Gif reactions, we also tested in our systems the effect of addition of this free acid. However, no appreciable effect was detected on adding a ten-fold excess (relatively to the catalyst) to the reaction mixture with either the most active complex **4** (compare entry 14 with entry 10, Table 3) or one of the least active ones, compound **1** (compare entry 16 with entry 15). Hence, the effect of picolinic acid is recognized only when coordinated to a metal centre as in **4**. Although complex **5** contains an aromatic N,O ligand similar to picolinate in **4**, it is one of the most inactive catalysts; the steric hindrance associated to the methyl ester group (Fig. 4) may play a deactivating role.

The isolation and full characterization of intermediates in the reactions were attempted but still remain elusive and therefore the mechanisms are unclear. In principle, they can involve intermediate oxo and peroxo complexes and, in this respect, it is noteworthy to mention that the peroxomethylrhenium(VII) complex $[(\text{Me})\text{ReO}(\text{O}_2)_2]$ is the active species of the known $[(\text{Me})\text{ReO}_3]/\text{H}_2\text{O}_2$ system in olefin and aromatic oxidations.^[1c, d] Other high valent peroxo-Re complexes are also known, such as $[(\text{Me})\text{ReO}(\text{O}_2)_2\text{H}_2\text{O}]$,^[34a] $[(\text{Me})\text{ReO}(\text{O}_2)_2\{\text{O}=\text{P}(\text{NMe}_2)_3\}]$,^[34b] $[\text{H}_4\text{Re}_2\text{O}_{13}]$,^[34c] and $[\text{ReCl}_2(\text{O}_2)(\text{NNCOOMe})(\text{PPh}_3)_2]$.^[34d] The reactions can proceed^[4d,13,14] via either (i) hydrogen atom abstraction from ethane (formation of ethyl radical) or (ii) electrophilic attack of a highly oxidized Re centre to a C–H bond of this substrate with resulting heterolytic cleavage and formation of an ethylrhenium species.

However, the ability of these Re complexes to either abstract the hydrogen atom from an alkane C–H bond or to abstract R^- from an alkane RH (mechanisms i or ii, respectively), to the best of our knowledge, has not yet been demonstrated. Although this cannot definitely rule out the involvement of such complexes in the catalytic process, it nevertheless points to the possibility of an alternative mechanism based on the metal-assisted thermolytic decomposition^[9g] of peroxodisulfate (or peroxodisulfuric acid, $\text{H}_2\text{S}_2\text{O}_8$, formed from $\text{K}_2\text{S}_2\text{O}_8$ in the acidic CF_3COOH medium) to the sulfate radical $\text{SO}_4^{\cdot-}$ (or $\text{HSO}_4^{\cdot}$ in acidic medium) which could behave as the H atom abstractor from ethane to give the ethyl radical. The capacity of the sulfate radical for hydrogen abstraction reactions from alkanes, including ethane, has already been clearly recognized and the rate constants have even been determined.^[35] This radical mechanism (i) should involve both carbon-centred and oxygen-centred radicals and is supported by the observation that when the reaction is carried out in the presence of either a C- or an O-centred radical trap, like CBrCl_3 , TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl), Ph_2NH or 2,6-di-*tert*-butyl-4-methylphenol (BHT),^[36] the yields of the acid products become negligible (entries 17–20, Table 3). In the carboxylation process, the ethyl radical would yield the acyl radical ($\text{EtCO}^{\cdot}$) which, upon oxidation and reaction with CF_3COOH (TFA), would form the mixed anhydride $\text{CF}_3\text{COOCOEt}$ that, on further reaction with CF_3COOH , would generate propionic acid (EtCOOH) and trifluoroacetic anhydride ($\text{CF}_3\text{COOCOCF}_3$). This follows a related proposal^[14] for methyl radical reactions.

Alternatively to the carbonylation, the ethyl radical can also be oxidized by the peroxodisulfate to yield acetic acid,^[13b] and the latter reaction predominates over the former for sufficiently low CO pressures.

It is also noteworthy to mention that our reactions are not expected to involve, as intermediates, either free propanol or free ethanol, or, as a carbonylating agent, CO_2 (a possible product of TFA decomposition), since these alcohols are not converted significantly into the carboxylic acids (only ethanol gives, in very low yield, acetic acid) and the acid yields do not increase in the presence of that gas. The N,O chelating ligands, in our systems, can probably be involved (upon decoordination of one N or O atom) in proton-transfer steps as postulated^[8,16,17a,33,37] in other alkane oxidation systems.

Replacement of TFA, as the solvent, by acetic acid or trichloroacetic acid results in the loss of activity of the systems. These are also inactive for the carboxylation of methane to acetic acid.

The carboxylation of ethane into propionic and acetic acid is still very little explored.^[10–14] Most of the published works report only single experiments, with the exception of one study^[13a] on the $\text{Pd}(\text{OAc})_2/\text{Cu}(\text{OAc})_2$ system for which various factors of the catalytic activity were investigated. In order to compare our results with those

Table 4. Comparison of activities of transition metal catalysts towards ethane carboxylation.^[a]

Catalyst	<i>p</i> C ₂ H ₆ [atm]	<i>p</i> CO [atm]	Yield ^[b]			TON ^[d]	Ref.
			Propionic acid	Acetic acid	Total ^[c]		
Co(OAc) ₂	10	30	0.4	2.7	3.1	2.3	[11,12]
Pd(OAc) ₂ /Cu(OAc) ₂	30	20	2.1	–	2.1	25.3	[13a]
Pd(OAc) ₂ /Cu(OAc) ₂	1	20	17.7	–	17.7	11.0	[13a]
Re complex 4	10	30	23.8	5.2	29.0	44.5	This work

^[a] K₂S₂O₈ and TFA were used as oxidant and solvent, respectively.

^[b] Moles of product/100 moles of ethane.

^[c] Propionic acid + acetic acid.

^[d] Moles of products (propionic acid + acetic acid)/mol of catalyst.

previously reported with other transition metal catalysts, we considered the best quoted yields and TONs, when available (Table 4). Cobalt(II) acetate exhibits a low activity with a total yield and TON of 3.1% and 2.3, respectively.^[11,12] A better TON of 25.3 (based on the total of both atoms) was achieved^[13a] for the above mixed Pd(II)/Cu(II) catalyst, but with a low yield (2.1%) which, in order to increase it considerably (to 17.7%), required the marked reduction of ethane pressure to 1 atm. In view of the reported^[10] activity of CaCl₂ (although with a much lower TON, 1.3, and with a high yield also requiring the low atmospheric pressure of C₂H₆), we have also tested that salt for ethane pressures of 1 and 10 atm (in both cases at a CO pressure of 30 atm) but obtained rather modest results, i.e., only traces of propionic acid were detected with acetic acid yields of 18.4% and 3.6%, and low TONs of 0.3 and 5.5, respectively.

Hence, our system with the Re complex **4** catalyst, to the best of our knowledge, is the most active one so far reported for ethane carboxylation.

Conclusion

The study shows that (i) inorganic oxorhenium(V) complexes with N,O ligands such as picolinate and iminoacetates, like those of the present study, can be conveniently prepared from the oxochloro starting material [ReOCl₃(PPh₃)₂] and (ii) are particularly promising sources of active catalysts for the single-pot ethane carboxylation under rather mild conditions and with remarkable yields of propionic acid. The picolinate complex provides, according to our best knowledge, the most active system so far reported not only for the carboxylation of ethane but also, in general, for the functionalization of any alkane by using an Re coordination compound as a catalyst. In the unique previously reported^[2i,5] cases of Re-catalyzed alkane oxidations, i.e., the peroxidative oxidation of cyclohexane, only rather low yields were achieved: 1.5% (although with a TON of 126) by the [(Me)ReO₃]/pyrazine-2-carboxylic acid/anhydrous H₂O₂ system, in refluxing acetonitrile at 80 °C,^[2i] and a maximum of 2.4% by the benzoyldiazenido-rhenium

complexes/aqueous H₂O₂/MeCN system at room temperature.^[5]

The synthetic process we have achieved in this work for propionic acid has some considerable advantages over those normally used in industry^[15a] for its manufacture, although using a more expensive oxidizing agent. In fact, it (i) either proceeds under much milder conditions (e.g., the industrial ethylene carbonylation process normally requires temperatures above 250 °C and pressures above 100 atm, and the air oxidation of naphtha operates at *ca.* 170 °C and above 40 atm) or (ii) is more direct and simple (e.g., than the two-stage process *via* the production of propanal by high pressure and high temperature hydroformylation of ethylene, followed by oxidation of that aldehyde; or than the production of propionic acid as a secondary product in the three-stage Monsanto or Cativa processes for acetic acid, the first two stages operating under drastic conditions, whereas the third one, i.e., the carboxylation of alcohol requires an expensive Rh or Ir catalyst), or (iii) is more selective (e.g., the naphtha oxidation process leads to a product mixture with a low proportion, *ca.* 10–15%, of propionic acid).

We expect that the investigation will be extended to other alkanes and reactions, and to different rhenium catalysts, oxidizing agents and solvents, with attempts to isolate intermediates, thus allowing the expansion of the still underdeveloped rhenium-based catalysis and the establishment of a single-pot functionalization process of gaseous alkanes under mild or moderate conditions with potential commercial value.

Experimental Section

General Materials and Procedures

All synthetic work was performed under a dinitrogen atmosphere using standard Schlenk techniques. The solvents were dried and degassed by standard methods. Potassium perhenate (Merck), triphenylphosphine (Aldrich), *N,N*-bis(2-hydroxyethyl)glycine (bicine) (Aldrich), *N*-(2-hydroxyethyl)iminodiacetic acid (Aldrich), picolinic acid (Aldrich) and 2,6-pyridinedicarboxylic acid (Aldrich) were obtained from commercial

sources and used as received. Oxotrichlorobis(triphenylphosphine)rhenium(V) $[\text{ReOCl}_3(\text{PPh}_3)_2]$ (**1**) was prepared by a published method.^[19]

C, H and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. Melting points were determined on a Köffler table. Positive-ion FAB mass spectra were obtained on a Trio 2000 instrument by bombarding 3-nitrobenzyl alcohol (NBA) matrices of the samples with 8 keV (ca. $1.18 \cdot 10^{15}$ J) Xe atoms. Mass calibration for data system acquisition was achieved using CsI. Infrared spectra ($4000\text{--}400\text{ cm}^{-1}$) were recorded on a Jasco FT/IR-430 instrument in KBr pellets. ^1H , $^{31}\text{P}\{^1\text{H}\}$ and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were measured on a Varian UNITY 300 spectrometer at ambient temperature. The ^{31}P chemical shifts are relative to external 85% H_3PO_4 solution.

Preparation of $[\text{ReOCl}(\text{OCH}_2\text{CH}_2)\text{N}(\text{CH}_2\text{CH}_2\text{OH})(\text{CH}_2\text{COO})](\text{PPh}_3)_2$ (**2**)

To a suspension of **1** (300 mg, 0.36 mmol) in 30 mL of MeOH an excess of bicine (176 mg, 1.08 mmol) was added and the reaction mixture was refluxed for 10 min. The resulting purple clear solution was taken to dryness under reduced pressure to give a purple residue to which 10 mL MeOH were added. The white solid that separated out from the resulting solution was filtered off and discarded. The filtrate was evaporated under reduced pressure to give a purple residue which was treated with 30 mL Et_2O to yield a solid. It was filtered off, washed with Et_2O and dissolved in 20 mL CH_2Cl_2 to form a cloudy solution. Filtration followed by concentration under reduced pressure yielded a purple oil. The addition of Et_2O (20 mL) led to the precipitation of a solid which was filtered off, washed with Et_2O ($3 \times 10\text{ mL}$) and dried under vacuum to afford complex **2** as a light purple powder; yield: 100 mg (42%, based on **1**). Product **2** is soluble in MeOH, Me_2CO , CH_2Cl_2 , CHCl_3 and MeCN; mp 158°C (dec.); anal. calcd. for $\text{C}_{24}\text{H}_{26}\text{ClNO}_5\text{PRe}$ (MW 661): C 43.60, H 3.96, N 2.12; found: C 43.80, H 4.28, N 1.91; FAB⁺-MS: $m/z = 661$ $[\text{M}]^+$, 641 $[\text{M} - \text{HCl} + \text{O}]^+$, 625 $[\text{M} - \text{HCl}]^+$, 596 $[\text{M} - \text{Cl} - \text{EtO} + \text{O}]^+$, 580 $[\text{M} - \text{Cl} - \text{EtO}]^+$, 319 $[\text{M} - \text{Cl} - \text{EtO} - \text{PPh}_3 + \text{H}]^+$. IR (selected bands): $\nu = 3364\text{ s br } \nu(\text{OH})$, 3059 m, 2943 m $\nu_{\text{as}}(\text{CH})$, 2868 m $\nu_s(\text{CH})$, 1650 s br $\nu_{\text{as}}(\text{COO})$, 1436 s $\nu_s(\text{COO})$, 1096 s $\nu(\text{C}=\text{O})$, 957 s $\nu(\text{Re}=\text{O})\text{ cm}^{-1}$; ^1H NMR (CDCl_3): $\delta = 7.73\text{--}7.37$ (m, 15H, PPh_3), 4.64 (q, $J = 5.4\text{ Hz}$, 2H, CH_2), 4.36–3.95 (m, 6H, CH_2), 3.39–2.92 (m, 2H, CH_2); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 188.15$ ($\text{C}=\text{O}$), 134.75–128.54 (m, PPh_3), 72.27, 69.11, 64.57, 63.23 and 59.35 (CH_2); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 2.67$ (s). X-ray quality crystals were grown by slow evaporation at 5°C of a CH_2Cl_2 -MeOH solution of **2**.

Preparation of $[\text{ReOCl}(\text{OCH}_2\text{CH}_2)\text{N}(\text{CH}_2\text{COO})(\text{CH}_2\text{COOCH}_3)](\text{PPh}_3)_2$ (**3**)

A mixture of **1** (300 mg, 0.36 mmol) and *N*-(2-hydroxyethyl)-iminodiacetic acid (191 mg, 1.08 mmol) was refluxed in MeOH (30 mL) for 30 min to give a grayish purple suspension. It was filtered off, washed with MeOH ($3 \times 15\text{ mL}$) and dried under vacuum to afford complex **3** as a purple microcrystalline solid; yield: 179 mg (72% based on **1**). The filtrate was taken to dryness under reduced pressure to give a purple residue. The

addition of MeOH (10 mL) led to the precipitation of a solid which was filtered off, washed with MeOH ($3 \times 5\text{ mL}$) and dried under vacuum, to give the second crop of **3**; yield: 20 mg (8%, i.e., a total isolated yield of 80%). Product **3** is soluble in MeOH, CH_2Cl_2 , CHCl_3 (slightly) and MeCN (slightly); mp 188°C (dec.); anal. calcd. for $\text{C}_{25}\text{H}_{26}\text{ClNO}_6\text{PRe}$ (MW 689): C 43.57, H 3.80, N 2.03; found: C 43.51, H 4.01, N 2.05; FAB⁺-MS: $m/z = 654$ $[\text{M} - \text{Cl}]^+$, 640 $[\text{M} - \text{Cl} - \text{Me} + \text{H}]^+$, 516 $[\text{ReOCl}(\text{PPh}_3) + \text{O}]^+$; IR (selected bands): $\nu = 3059\text{ w}$, 2952 w $\nu_{\text{as}}(\text{CH})$, 2872 w $\nu_s(\text{CH})$, 1743 s $\nu_{\text{as}}(\text{COOMe})$, 1672 s $\nu_{\text{as}}(\text{COO})$, 1434 s $\nu_s(\text{COO})$, 1341 s $\nu_s(\text{COOMe})$, 1095 s $\nu(\text{C}=\text{O})$, 957 s $\nu(\text{Re}=\text{O})\text{ cm}^{-1}$; ^1H NMR (CDCl_3): $\delta = 7.78\text{--}7.45$ (m, 15H, PPh_3), 5.05–4.51 (m, 4H, CH_2), 4.13–3.93 (m, 2H, CH_2), 3.84 (s, 3H, CH_3), 3.72–3.26 (m, 2H, CH_2); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 191.08$ ($\text{C}=\text{O}$), 169.35 (COOMe), 135.07–128.13 (m, PPh_3), 72.43, 67.78, 63.74 and 62.32 (CH_2), 52.38 (CH_3); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 3.75$ (s). X-ray quality crystals were grown by slow evaporation at 5°C of a CH_2Cl_2 -MeOH solution of **3**.

Preparation of $[\text{ReOCl}_2\{\text{C}_5\text{H}_4\text{N}(\text{COO}-2)\}(\text{PPh}_3)]$ (**4**)

To a suspension of **1** (300 mg, 0.36 mmol) in 30 mL of MeOH an excess of picolinic acid (133 mg, 1.08 mmol) was added and the reaction mixture was refluxed for 1 h. The resulting deep red clear solution was concentrated under reduced pressure to give a red oil which was treated with 15 mL CH_2Cl_2 . The solid that separated out from the resulting solution was filtered off and discarded. The filtrate was evaporated under reduced pressure giving a red oil which was dissolved in 30 mL Et_2O to form a red precipitate. It was filtered off, washed by Et_2O ($3 \times 10\text{ mL}$) and dissolved on a filter in 15 mL CH_2Cl_2 to form a deep red solution which was taken to dryness under reduced pressure yielding a deep red oil. The addition of Et_2O (30 mL) led to the formation of a solid which was filtered off, washed with Et_2O ($3 \times 10\text{ mL}$) and dried under vacuum to give complex **4** as a reddish purple microcrystalline material; yield: 206 mg (87% based on **1**). Product **4** is soluble in MeOH, Me_2CO , CH_2Cl_2 , CHCl_3 , C_6H_6 and MeCN; mp 223°C (dec.); anal. calcd. for $\text{C}_{24}\text{H}_{19}\text{Cl}_2\text{NO}_3\text{PRe}$ (MW 657.5): C 43.84, H 2.91, N, 2.13; found: C 44.02, H 2.96, N 2.03; FAB⁺-MS $m/z = 658$ $[\text{M} + \text{H}]^+$, 622 $[\text{M} - \text{Cl}]^+$, 587 $[\text{M} - 2\text{Cl}]^+$, 553 $[\text{M} - \{\text{C}_5\text{H}_4\text{NCOO}\} + \text{H}_2\text{O}]^+$, 535 $[\text{M} - \{\text{C}_5\text{H}_4\text{NCOO}\}]^+$, 499 $[\text{M} - \{\text{C}_5\text{H}_4\text{NCOO}\} - \text{HCl}]^+$, 447 $[\text{Re}(\text{PPh}_3)_2 - 2\text{H}]^+$; IR (selected bands): $\nu = 3056\text{ m}$, 2971 w $\nu_{\text{as}}(\text{CH})$, 2874 w $\nu_s(\text{CH})$, 1704 s $\nu_{\text{as}}(\text{COO})$, 1436 s $\nu_s(\text{COO})$, 988 s $\nu(\text{Re}=\text{O})\text{ cm}^{-1}$; ^1H NMR (CDCl_3): $\delta = 8.93$ (t, $J = 7.5\text{ Hz}$, 1H, PyH), 8.73 (t, $J = 7.4\text{ Hz}$, 1H, PyH), 8.54–7.10 (m, 15H, PPh_3 + 2H, PyH); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 163.36$ ($\text{C}=\text{O}$), 148.10, 143.73, 137.63, 127.66 and 125.35 (PyC), 134.03–128.30 (m, PPh_3); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = -10.80$ (s). X-ray quality crystals were grown at 5°C by vapor diffusion of *n*- C_5H_{12} into a CH_2Cl_2 or a C_6H_6 - Me_2CO solution of **4**.

Preparation of $[\text{ReOCl}_2\{\text{C}_5\text{H}_3\text{N}(\text{COOCH}_3-2)(\text{COO}-6)\}(\text{PPh}_3)]$ (**5**)

A mixture of **1** (300 mg, 0.36 mmol) and 2,6-pyridinedicarboxylic acid (180 mg, 1.08 mmol) was refluxed in MeOH (50 mL) for about 6 h to produce a greenish brown suspension. It was

filtered off, washed with MeOH (3×15 mL) and dried under vacuum to afford complex **5** as a greenish grey microcrystalline solid; yield: 136 mg (53% based on **1**). Product **5** is soluble in Me₂CO, CH₂Cl₂, MeCN, CHCl₃ (slightly) and C₆H₆ (slightly); mp 168 °C; anal. calcd. for C₂₆H₂₁Cl₂NO₅PRE (MW 715.5): C 43.64, H 2.96, N 1.96; found: C 43.96, H 3.14, N 1.79; FAB⁺-MS: m/z = 715 [M]⁺, 679 [M – HCl]⁺, 628 [M – 2Cl – OH]⁺, 613 [M – Cl – MeOH]⁺; IR (selected bands): ν = 3042 w, 2912 w ν (CH), 1744 s ν_{as} (COOMe), 1707 s ν_{as} (COO), 1437 s ν_s (COO), 1334 s ν_s (COOMe), 1001 s ν (Re=O) cm^{–1}; ¹H NMR (CDCl₃): δ = 7.88–7.35 (m, 18H, PPh₃ + PyH), 3.66 (s, 3H, CH₃); ¹³C{¹H} NMR (CDCl₃): δ = 187.86 (C=O), 176.83 (COOMe), 142.58, 138.20, 127.88, 126.66 and 126.26 (PyC), 134.25–128.80 (m, PPh₃), 53.39 (CH₃); ³¹P{¹H} NMR (CDCl₃): δ = –11.83 (s). X-ray quality crystals were grown by slow evaporation at 5 °C of a CH₂Cl₂ solution of **5**.

X-Ray Crystal Structure Determinations

The X-ray diffraction data were collected with a Nonius Kappa CCD diffractometer using Mo-K α radiation. The Denzo-Scalepack program package^[38] was used for cell refinements and data reductions. All structures were solved by direct methods using the SIR97 or SIR2002 programs^[39] with the WinGX graphical user interface.^[40] An empirical absorption correction was applied to all data (T_{min}/T_{max} : 0.07136/0.11199, 0.5226/0.8207, 0.2585/0.6058, 0.3878/0.6521 for **2–5**, respectively) using XPRED in SHELXTL v.6.12 program.^[41] Structural refinements were carried out with SHELXL-97.^[42] All hydrogens were placed in idealized positions and constrained to ride on their parent atom.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-239092 (**2**), CCDC-239093 (**3**), CCDC-239094 (**4**), CCDC-239095 (**5**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

Catalytic Activity Studies

Ethane (AlphaGaz), carbon monoxide (Air Products) and dinitrogen gases (Air Liquid Portugal), potassium peroxodisulfate (Fluka), trifluoroacetic acid (Aldrich), CBrCl₃ (Fluka), 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) (Aldrich), Ph₂NH (Fluka), 2,6-di-*tert*-butyl-4-methylphenol (BHT) (Aldrich) and *n*-butyric acid (Aldrich) were obtained from commercial sources and used as received. The reaction mixtures were prepared as follows. To 0.01–0.02 mmol of the Re complex **1**, **2**, **3**, **4** or **5** contained in a 13.0-mL stainless steel autoclave equipped with a Teflon-coated magnetic stirring bar were added 4 mmol (1.08 g) K₂S₂O₈ and 5 mL of TFA. Then the autoclave was closed and flushed with dinitrogen three times for removing the air and finally pressurized with 5–15 atm of ethane and 0–40 atm of carbon monoxide. The reaction mixture was vigorously stirred for 20 h at 80 °C using a magnetic stirrer and an oil bath. After the reaction was complete, the autoclave was cooled in an ice bath, then degassed and opened. To 1 mL of the reaction mixture were added

5 mL of diethyl ether and 90 μ L of *n*-butyric acid (as internal standard). The obtained mixture was stirred, then filtered off and analyzed by gas chromatography using a Fisons Instruments GC 8000 series gas chromatograph with a DB WAX fused silica capillary column (P/N 123–7032) and the JASCO-BORWIN v.1.50 software. In some cases, products were also identified by GC-MS, ¹H and ¹³C{¹H} NMR techniques.

Blank experiments were performed in the absence of metal complex catalyst or of K₂S₂O₈. Propionic acid was never detected and only traces (below 0.5%) of acetic acid were revealed in the presence of this peroxo reagent but without the metal complex.

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