

Preparation and Crystal Structures of Benzoylhydrazido- and -diazenidorhenium Complexes with N,O-Ligands and Their Catalytic Activity Towards Peroxidative Oxidation of Cycloalkanes

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The η^2 -(benzoylhydrazido)rhenium(V) complex $[\text{Re}\{(\text{OCH}_2\text{CH}_2)_2\text{N}(\text{CH}_2\text{CH}_2\text{OH})\}\{\text{N}=\text{NC}(\text{O})\text{Ph}\}(\text{PPh}_3)]$ (**2**) and the η^1 -(benzoyldiazenido)rhenium(III) compounds $[\text{ReCl}\{\text{N}(\text{CH}_2\text{COO})(\text{CH}_2\text{CH}_2\text{OH})(\text{CH}_2\text{CH}_2\text{OH})\}\{\text{N}=\text{NC}(\text{O})\text{Ph}\}(\text{PPh}_3)]$ (**3**) and $[\text{ReCl}(\text{O},N\text{-L})\{\text{N}=\text{NC}(\text{O})\text{Ph}\}(\text{PPh}_3)_2]$ [$\text{O},N\text{-L} = \text{N}(\text{O})\text{-CH}_2\text{COO}$ (**4**), $\text{HN}=\text{C}(\text{Me})\text{COO}$ (**5**), $\text{C}_5\text{H}_4\text{N}(\text{COO})$ (**6**)], with chelating N,O-ligands (amino alkoxides, amino-, oxyamino-, imino- and pyridinocarboxylates) have been prepared by treatment of $[\text{ReCl}_2\{\text{N}=\text{NC}(\text{O})\text{Ph}\}(\text{PPh}_3)_2]$ (**1**) with triethanolamine $[\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3]$, *N,N*-bis(2-hydroxyethyl)glycine $[\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2(\text{CH}_2\text{COOH})]$, *N*-hydroxyiminodiacetic acid $[\text{HON}(\text{CH}_2\text{COOH})_2]$, *N*-hydroxy-2,2'-iminodipropionic acid $[\text{HON}[\text{CH}(\text{Me})\text{COOH}]_2]$ and picolinic acid $[\text{NC}_5\text{H}_4\text{COOH-2}]$, respectively. The N,O-ligands in **4** and **5** result from fragmentation of the *N*-hydroxyiminodicarboxylic acids. All the com-

plexes have been characterized by IR, ^1H and ^{13}C NMR spectroscopy, FAB⁺-MS, elemental analysis and X-ray diffraction structural analysis, which indicate a π -delocalized chelated benzoylhydrazidorhenium ring in **1** and **2**, and, in the other complexes, an essentially linear η^1 -diazenido ligand that is always *trans* to the O-coordinated carboxylate moiety of the N,O-ligand. The complexes act as catalysts (TON values up to about 45) for peroxidative oxidation, by radical mechanisms, of cyclohexane and cyclopentane to the corresponding alcohols and ketones, under mild conditions (room temperature, use of aqueous H_2O_2 and without added acid). This is an unprecedented use of inorganic Re coordination compounds as catalysts in alkane functionalization.

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Introduction

The coordination chemistry of rhenium^[1] is a field of current growing interest from various viewpoints, especially for improving fundamental knowledge (e.g. on structural and physicochemical properties and on reactivity) and in topics with an applied character such as the development of diagnostic/radiotherapeutic cancer agents,^[2,3] nitrogen fixation (a good number of Re dinitrogen and formally derived organodiazido-type complexes are known)^[4–13] and catalysis.^[14–24]

For the synthesis of diazenido and dinitrogen complexes with phosphorus-containing coligands, the benzoylhydrazide complex $[\text{ReCl}_2\{\text{N}=\text{NC}(\text{O})\text{Ph}\}(\text{PPh}_3)_2]$ (**1**) is a key starting material,^[25–28] but its use as a precursor for complexes with N-based coligands is still very rare and is usu-

ally limited to amines.^[29–31] Hence, one of the aims of this work is to extend the application of complex **1** to the synthesis of benzoyldiazenido complexes with coligands of the latter type.

Another objective of this study is to find catalytic applications of such complexes, thus providing a contribution towards widening the field of catalysis with inorganic coordination compounds of rhenium, which still remains little explored.^[32–41] This contrasts with the recently discovered catalytic behaviour of high-valent organorhenium oxides,^[14–24] in particular the methyltrioxide $[(\text{Me})\text{ReO}_3]$, whose catalytic behaviour has been extensively studied for a variety of processes, such as epoxidation and hydroxylation of olefins, oxidation of alkynes, aromatic hydrocarbons, sulfides, amines, silanes, alcohols and ketones, and cyclization reactions.

As the catalytic reaction to be tested, we chose the oxidation of cyclohexane and of cyclopentane to the corresponding alcohols and ketones, as examples with industrial significance within the challenging field of functionalization of alkanes.^[42–47] In fact, the cyclohexanol/cyclohexanone mixture is used^[42,48–50] for the synthesis of adipic acid, Nylon-6,6', polyamide-6 and urethane foams and as an acidulant in baking powder and lubricating additives, whereas cyclopentanol and cyclopentanone are used^[51–57] in the

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preparation of perfumes, dibasic carboxylic acids, dyes and liquid herbicide compositions. We have previously found that the peroxidative oxidation of cyclohexane and cyclopentane to those products is catalyzed by some vanadium(IV) or (V) complexes with N,O-ligands,^[58] as well as by heteronuclear iron(III)–chromium(III) hydroxo complexes and hydroxides.^[59]

For the current study, as sources of N-ligands we have addressed N,O-types (or related compounds) that we have used for the preparation of vanadium catalysts for alkane functionalization reactions, namely peroxidative hydroxylation, oxygenation and halogenation,^[58] and carboxylation.^[60] They are the amino alcohol $N(\text{CH}_2\text{CH}_2\text{OH})_3$, the glycine derivative $N(\text{CH}_2\text{CH}_2\text{OH})_2(\text{CH}_2\text{COOH})$, picolinic acid ($\text{NC}_5\text{H}_4\text{COOH}-2$), *N*-hydroxyiminodiacetic acid [$\text{HON}(\text{CH}_2\text{COOH})_2$, HIDA] and *N*-hydroxy-2,2'-iminodipropionic acid [$\text{HON}\{\text{CH}(\text{Me})\text{COOH}\}_2$, HIDPA].

Hence, we report herein the synthesis and characterization, including the crystal structures, of a series of new benzoylhydrazido- and -diazenidorhenium complexes with these, or derived, chelating N,O-ligands, as well as their catalytic activity for the peroxidative oxidation under mild conditions (room temperature, aqueous H_2O_2 and without added acid) of cyclohexane and cyclopentane to the corresponding alcohols and ketones, which, to the best of our knowledge, is the first example of such a type of alkane functionalization with Re coordination compounds as catalysts.

Results and Discussion

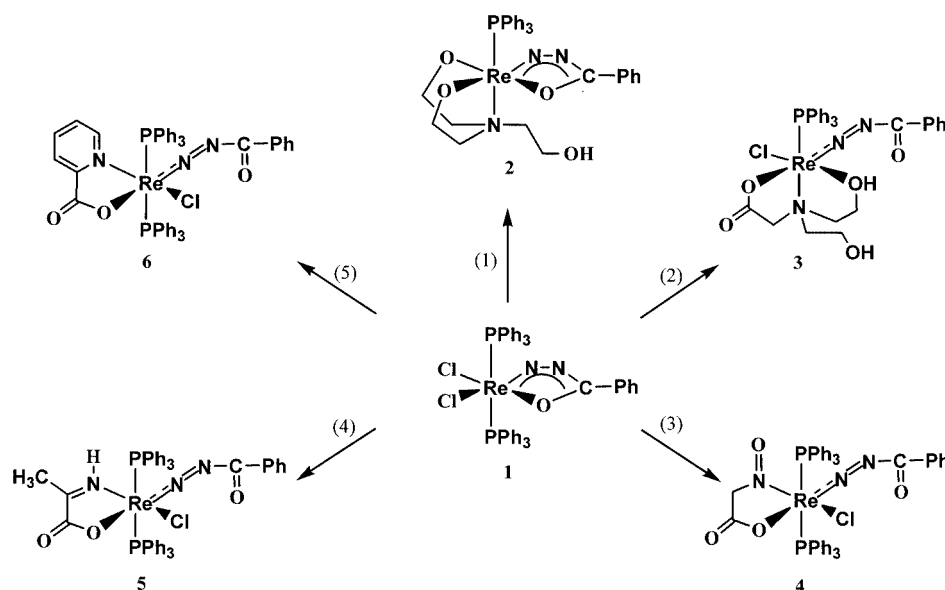
Synthesis and Spectroscopic Characterization

The reaction of the benzoylhydrazido chelate **1** with various potential N,O-polydentate ligands in refluxing meth-

anol led to the formation of neutral benzoylhydrazido (**2**) and diazenido (**3–6**) complexes, in 30–55% yields, as shown in Scheme 1. All complexes were characterized by IR, FAB⁺-MS, ¹H and ¹³C{¹H} NMR spectroscopy, elemental analysis and single-crystal X-ray diffraction analysis.

In the reaction of **1** with triethanolamine (reaction 1, Scheme 1) the latter, upon deprotonation of two alcohol moieties, provides a dianionic tridentate N,O,O-ligand that replaces one triphenylphosphane and two chloride ligands, with preservation of the chelated benzoylhydrazido fragment in the green product $[\text{Re}\{(\text{OCH}_2\text{CH}_2)_2\text{N}-(\text{CH}_2\text{CH}_2\text{OH})\}\{\text{N}=\text{NC}(\text{O})\text{Ph}\}(\text{PPh}_3)]$ (**2**). *N,N*-Bis(2-hydroxyethyl)glycine [bicine, $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2(\text{CH}_2\text{COOH})$] also generates an N,O,O-ligand by deprotonation of the carboxylic acid group. Reduction of the metal to the +3 oxidation state also occurs, the chelated benzoylhydrazido ring opens to form the η^1 -NNCOPh diazenido ligand and only one ligated chloride is replaced (besides one of the phosphanes) to afford the greenish-blue complex $[\text{ReCl}\{\text{N}(\text{CH}_2\text{COO})(\text{CH}_2\text{CH}_2\text{OH})(\text{CH}_2\text{COOH})\}\{\text{N}=\text{NC}(\text{O})\text{Ph}\}(\text{PPh}_3)]$ (**3**) (reaction 2, Scheme 1). In complexes **2** and **3** the N,O,O-ligands contain hydroxyethyl arms, in agreement with the detection, in the IR spectra, of strong and broad bands in the 3500–3200 cm^{-1} range assigned to $\nu(\text{OH})$. The IR spectra of **3** and all the other benzoyldiazenido compounds show a strong band in the 1700–1630 cm^{-1} range assigned to $\nu(\text{C}=\text{O})$, whereas for all the complexes $\nu(\text{N}=\text{N})$, associated to either η^2 - or η^1 -NNC(O)Ph, is observed in the 1513–1436 cm^{-1} range.

In their reactions with complex **1**, the *N*-hydroxyiminodiacetic acids (HIDA and HIDPA) undergo fragmentation, leading to the formation of the $\text{O} \leftarrow \text{NCH}_2\text{COO}^-$ (*N*-oxyaminoacetate) and $\text{HN}=\text{C}(\text{Me})\text{COO}^-$ (2-iminopropionate) ligands in the η^1 -benzoyldiazenidorhenium(III) products $[\text{ReCl}\{\text{N}(\text{O})\text{CH}_2\text{COO}\}\{\text{N}=\text{NC}(\text{O})\text{Ph}\}(\text{PPh}_3)_2]$ (**4**)



Scheme 1. (1) $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$; (2) $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2(\text{CH}_2\text{COOH})$ (bicine); (3) $\text{HON}(\text{CH}_2\text{COOH})_2$ (HIDA); (4) $\text{HON}\{\text{CH}(\text{CH}_3)\text{COOH}\}_2$ (HIDPA); (5) $\text{NC}_5\text{H}_4\text{COOH}-2$.

$[\nu(\text{N}=\text{O}) = 1626 \text{ cm}^{-1}]$ and $[\text{ReCl}\{\text{HN}=\text{C}(\text{Me})\text{COO}\}\{\text{N}=\text{NC}(\text{O})\text{Ph}\}(\text{PPh}_3)_2]$ (**5**), respectively (reactions 3 and 4, Scheme 1). HIDPA fragmentations have been rarely characterized, although some examples^[61] are provided by the reaction with $[\text{PPh}_4][\text{ReOBr}_4]$, $[\text{ReOCl}_3(\text{PPh}_3)_2]$, $[\text{ReOCl}_2(\text{O-Et})(\text{PPh}_3)_2]$ or $[\text{PPh}_4][\text{MoOCl}_4(\text{H}_2\text{O})]$, leading to the formation of 2-[(1-carboxyethoxy)imino]propionic acid $[\text{HOOC}(\text{Me})=\text{N}\{\text{OCH}(\text{Me})\text{COO}^-\}]$, 2-iminopropionate $[\text{HN}=\text{C}(\text{Me})\text{COO}^-]$, 2,2'-iminodipropionate $[\text{HN}\{\text{CH}(\text{Me})\text{COO}^-\}_2]$ and 2-oxidoiminopropionic acid $[\text{HOOC}(\text{Me})=\text{N}\rightarrow\text{O}]$ ligands, respectively. The 2-iminopropionate ligand in **5** has a precedent in $[\text{PPh}_4][\text{ReOBr}_3\{\text{HN}=\text{C}(\text{Me})\text{COO}\}]$,^[61] whereas the *N*-oxyaminoacetate in **4** appears to result from a different type of HIDA fragmentation.

Similar to complexes **4** and **5**, the η^1 -benzoyldiazenidorhenium(III) product $[\text{ReCl}\{\text{C}_5\text{H}_4\text{N}(\text{COO})\}\{\text{N}=\text{NC}(\text{O})\text{Ph}\}(\text{PPh}_3)_2]$ (**6**) obtained from the reaction of picolinic acid with **1** (reaction 5, Scheme 1) also has an anionic bidentate N,O-ligand, in this case simply corresponding to the basic form of the acid reagent.

The molecular ions were clearly observed with the expected isotopic patterns in the FAB^+ -mass spectra of all compounds, except **3**. Other typical peaks correspond to the stepwise fragmentations by loss of Cl, N_2COPh , PPh_3 and N,O-ligand fragments. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra show resonances at the usual chemical shifts for the coordinated PPh_3 , N_2COPh and N,O-ligands.^[29–31,62–69] Elemental analyses are also consistent with the proposed formulations, which were authenticated by single-crystal X-ray diffraction studies, as indicated below.

X-ray Crystal Structures

Green single crystals of the starting material $\mathbf{1}\cdot\text{C}_6\text{H}_6$ were grown by slow evaporation at 5°C of an $\text{EtOH}/\text{C}_6\text{H}_6$ solution and the crystal structure was solved in order to compare its crystal data with those of the newly obtained complexes. The molecular structure of **1** (Figure 1) consists of discrete mononuclear species of distorted octahedral geometry with *trans* phosphane ligands and the other ligands in equatorial sites. Hence, the chloride ligands are *trans* to the nitrogen and carbonyl oxygen donors of the chelating benzoylhydrazido ligand. The bonding parameters (Table 1) are similar to those of the analogous complex $[\text{ReCl}_2\{\text{N}=\text{NC}(\text{O})\text{C}_6\text{H}_4\text{Cl-4}\}(\text{PPh}_3)_2]$.^[70]

All the other complexes also exhibit distorted octahedral coordinations and, for those with two phosphanes (**4–6**), these bulky ligands are *trans* to each other, as in complex **1**, in agreement with steric requirements.

In complex **2** (Figure 2), one triethanolamine is deprotonated at two oxygen atoms (O2, O3) and binds the metal through the amino-N and these atoms. The Re-N1 , Re-O1 , Re-P1 and N1-N2 distances (Table 1) are similar to those of **1**. Within the chelating benzoylhydrazide ligand, the short Re-N1 [1.776(5) and 1.798(3) Å in **1** and **2**, respectively] and N1-N2 [1.309(6) and 1.336(4) Å, respectively]

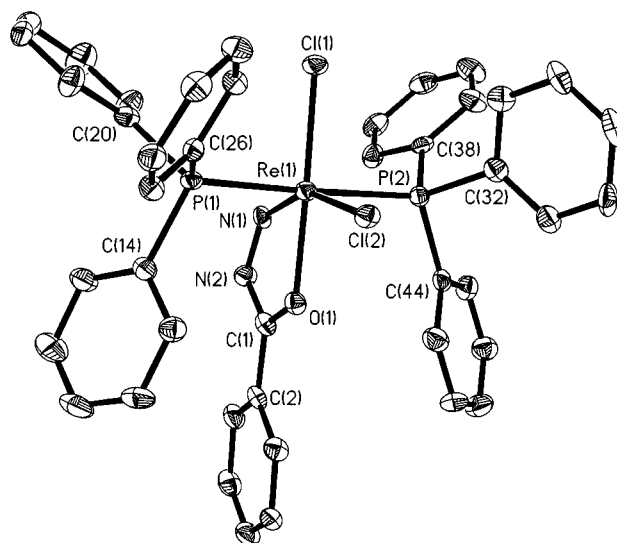


Figure 1. An ORTEP-3 representation of **1**. Hydrogen atoms and solvent molecule have been omitted for clarity.

bond lengths indicate significant multiple bonding character, and therefore a delocalized π -system, which is also in agreement with the Re-N1-N2 angles of $133.4(4)^\circ$ in **1** and $131.7(3)^\circ$ in **2**.^[70,71] According to a classification of organohydrazido ligands^[71] (assuming the convention that all electrons involved in the Re-N bond are donated by the hydrazine precursor), the benzoylhydrazido ligand in the chelates **1** and **2** exhibits features of both a hydrazido(3–) (**a**) and a diazenido(1–) (**b**) species.

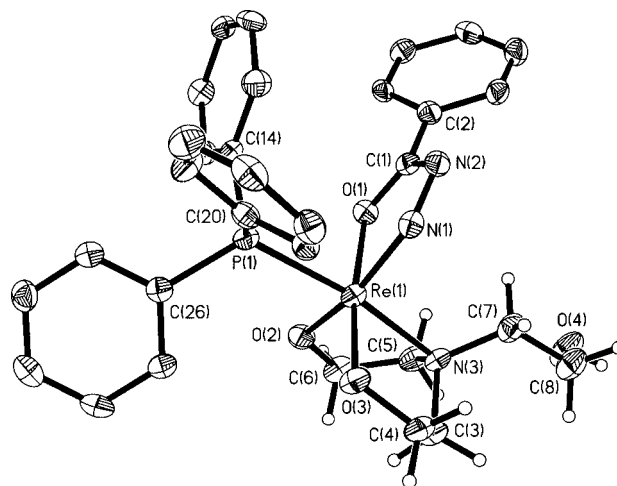
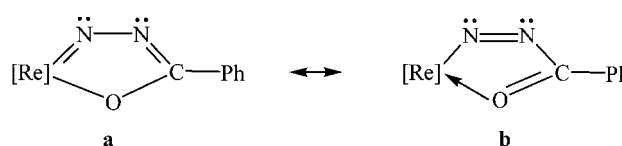


Figure 2. An ORTEP-3 representation of **2**. Ph hydrogen atoms have been omitted for clarity.



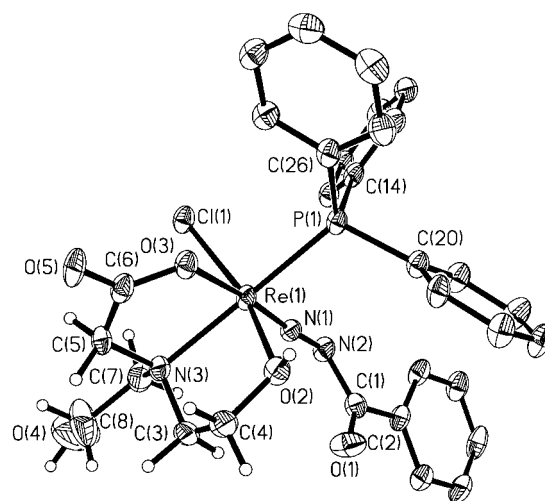
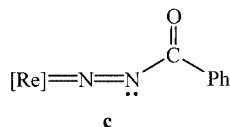
In **2** the Re-O2 and Re-O3 lengths of 1.94–1.97 Å are unexceptional for deprotonated oxygen atoms bonded to a metal centre, and are shorter than Re-O1 [2.170(3) Å]. The

Table 1. Selected bond lengths [Å] and angles [°] for compounds **1–6**.

	1	2	3	4	5	6
Re–N(1)	1.776(5)	1.798(3)	1.740(3)	1.734(7)	1.735(3)	1.745(6)
N(1)–N(2)	1.309(6)	1.336(4)	1.280(5)	1.264(9)	1.271(5)	1.259(9)
C(1)–N(2)	1.376(7)	1.358(5)	1.381(6)	1.408(11)	1.398(6)	1.396(11)
C(1)–O(1)	1.272(7)	1.279(5)	1.234(5)	1.234(11)	1.228(5)	1.211(11)
C(1)–C(2)	1.470(8)	1.469(6)	1.496(6)	1.476(12)	1.489(6)	1.482(13)
Re–O(1)	2.122(4)	2.170(3)				
Re–N(3)		2.217(3)	2.243(4)	2.078(8)	2.175(3)	2.109(7)
Re–O(2)		1.944(3)	2.119(3)	2.090(6)	2.089(3)	2.067(5)
Re–O(3)		1.974(3)	2.095(3)			
Re–Cl(1)	2.3723(14)		2.3948(10)	2.420(2)	2.4017(10)	2.409(2)
Re–Cl(2)	2.3672(14)					
Re–P(1)	2.4528(15)	2.3798(12)	2.3758(11)	2.475(2)	2.4438(8)	2.4660(16)
Re–P(2)	2.4654(15)			2.487(2)	2.4583(8)	2.4588(16)
C(3)–N(3)		1.497(5)	1.503(6)	1.470(12)	1.417(15)	
C(3)–C(4)		1.502(6)	1.489(7)	1.465(15)	1.577(16)	1.391(15)
C(4)–O(3)		1.434(5)		1.241(11)	1.223(5)	
C(4)–O(2)			1.456(5)	1.295(11)	1.305(5)	
N(3)–O(4)				1.246(14)		
Re–N(1)–N(2)	133.4(4)	131.7(3)	176.0(3)	169.3(6)	177.4(3)	168.3(6)
N(1)–N(2)–C(1)	104.3(5)	105.6(3)	115.7(3)	120.8(7)	115.2(3)	119.3(7)
O(1)–C(1)–N(2)	117.7(5)	119.0(4)	124.3(4)	124.0(8)	123.8(4)	124.1(8)
N(1)–Re–O(1)	71.48(18)	71.72(13)				
N(1)–Re–O(2)		152.65(14)	96.40(14)	176.4(3)	170.42(13)	168.0(2)
N(1)–Re–N(3)		98.67(13)	97.55(15)	99.6(3)	94.55(14)	92.7(3)
N(3)–Re–O(2)		79.51(12)	80.27(13)	77.6(3)	75.91(12)	75.4(2)
Re–N(3)–C(3)		103.9(2)	102.9(3)	113.8(6)	114.1(7)	
Re–O(2)–C(4)			113.1(3)	118.1(6)	121.4(2)	
P(1)–Re–P(2)	174.77(5)			178.11(7)	174.79(8)	175.9(7)
N(3)–Re–P(1)		171.06(9)	174.87(10)	90.1(2)	91.98(10)	89.5(3)
N(3)–Re–Cl(1)			89.25(10)	164.5(2)	164.87(9)	164.68(19)

binding of the triethanolamine ligand involves the chelate rings Re–N3–C3–C4–O3 and Re–N3–C5–C6–O2 with O3–Re–N3 and O2–Re–N3 bite angles of 82.14(12)° and 79.51(12)°, respectively. The Re–N3 bond [2.217(3) Å] is significantly longer than Re–O2 [1.944(3) Å] and Re–O3 [1.974(3) Å], as commonly observed for O,N,O- or N,O-donor ligands,^[61,72] and is also longer than the Re–N1 bond [1.798(3) Å], as anticipated for sp³ hybridization at the N3 site and sp² hybridization at N1, and in agreement with the appreciable double-bond character of the latter bond.

In the structures of **3–6** (Figures 3, 4, 5 and 6, respectively), the opening of the chelated benzoylhydrazido ring has occurred and the Re–N1–N2 angle of the resulting η¹-diazenido ligand is essentially linear [176.0(3)° in **3**, 169.3(6)° in **4**, 177.4(3)° in **5** and 168.3(6)° in **6**]. The Re–N1, N1–N2 and C1–O1 distances (Table 1) are slightly shorter than those in the η²-NNC(O)Ph ligand in **1** and **2**, which is indicative of a slight increase of the double-bond character. According to the above classification,^[71] the η¹-NNC(O)Ph ligand in compounds **3–6** exhibits features of a linear, four-electron donor diazenido(1–) (c). In all these complexes, this ligand adopts the position *trans* to the O-coordinated carboxylato group of the chelating N,O-ligand, in preference to being *trans* to any N, Cl or P atoms.

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

The bicine ligand in **3** involves the chelate rings Re–N3–C3–C4–O2 and Re–N3–C5–C6–O3, with O2–Re–N3 and O3–Re–N3 bite angles of 80.27(13)° and 78.84(12)°, respectively. The Re–N3(amine) distance of 2.243(4) Å (Table 1) is comparable with the corresponding one observed for complex **2**, although the Re–O2 and Re–O3 bond lengths of 2.119(3) and 2.095(3) Å are slightly longer than those in **2**.

In the structures of **4–6** (Figures 4, 5 and 6, respectively) most of the corresponding bond lengths and angles are sim-

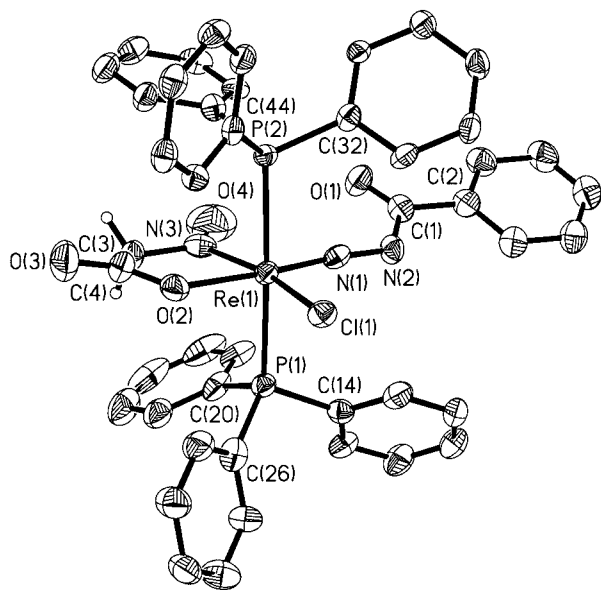


Figure 4. An ORTEP-3 representation of **4**. Ph hydrogen atoms have been omitted for clarity.

ilar (Table 1). Each N,O-ligand forms a chelate ring with a restricted O–Re–N bite angle, the N3 atom being always *trans* to the chloride and the O2 atom *trans* to the diazenido ligand. The Re–O2 and Re–N3 bond lengths are usually similar to those of other Re complexes.^[61,73] Hence, for example, for complex **6** most of the bond lengths are similar

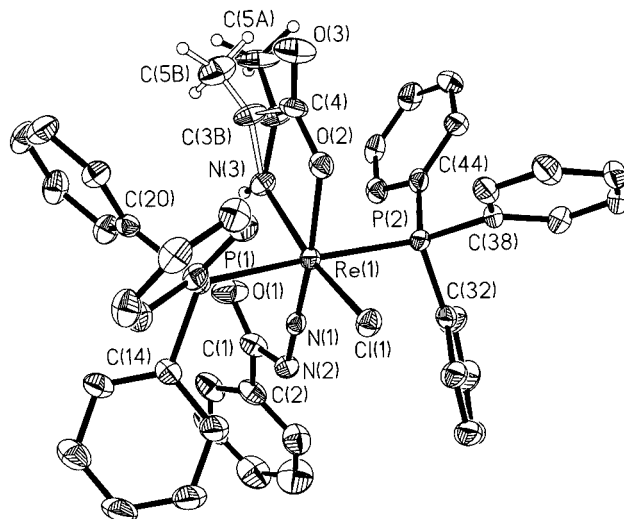


Figure 5. An ORTEP-3 representation of **5**. Ph hydrogen atoms and solvent molecules have been omitted for clarity.

to those of related complexes with picolinate or 3-hydroxypicolinate ligands such as $[\text{ReO}(\text{Me})(\text{NC}_5\text{H}_4\text{COO})_2]$, $[\text{ReH}(\text{NC}_5\text{H}_4\text{COO})_2(\text{PPh}_3)_2]$, $[\text{ReOI}_2\{\text{NC}_5\text{H}_3(\text{OH}-3)\text{COO}\}(\text{PPh}_3)]$ and $[\text{ReOCl}_3\{\text{NC}_5\text{H}_3(\text{OH}-3)\text{COO}\}]$.^[74–77] However, the Re–N3 bond length [2.175(3) Å] in **5** is longer than the Re–O2 distance [2.089(3) Å].

In the $\text{HN}=\text{C}(\text{CH}_3)\text{COO}^-$ ligand in **5**, the C3–N3 distance of 1.417(15) Å is much longer than the corresponding

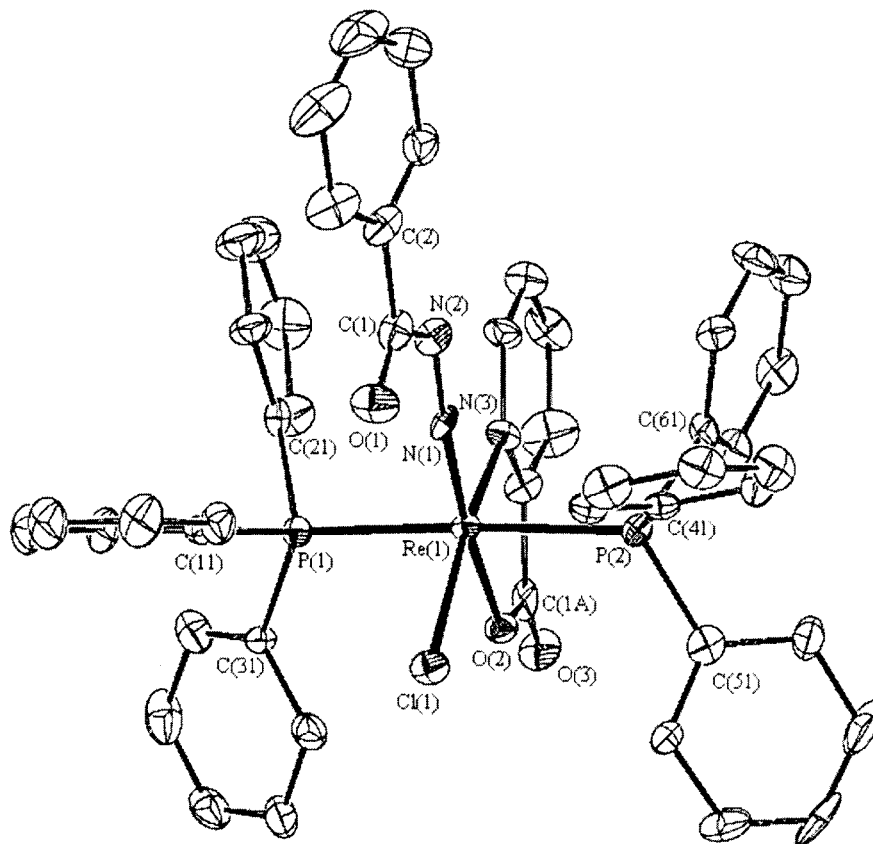
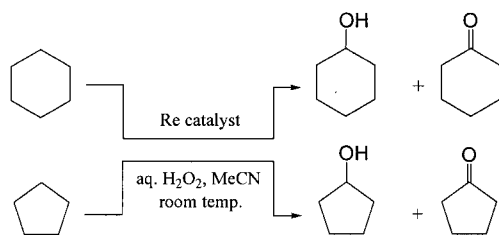


Figure 6. An ORTEP-3 representation of **6**. Hydrogen atoms and solvent molecule have been omitted for clarity.

C=N bond length in $[\text{PPh}_4][\text{ReOBr}_3\{\text{HN}=\text{C}(\text{Me})\text{COO}\}]$,^[61] even though the X-ray diffraction analysis shows that there is no hydrogen at the C3 atom.

Peroxidative Oxidation of Cyclohexane and Cyclopentane

Acetonitrile solutions of all our complexes **1–6** exhibit catalytic activity for the peroxidative oxidation of cyclohexane to the corresponding cyclohexanone and cyclohexanol at room temperature (see Scheme 2 and Table 2 for selected data and Table S1 in the Supporting Information). The amount of hydrogen peroxide has a strong effect, and increasing the peroxide-to-catalyst molar ratio within the 2000–32000 range leads to an enhancement of the turnover numbers (TONs); for example, the total TON when using complex **3** as a catalyst increases from 5 to 43 on increasing this ratio from 4000 to 32000 (Figure 7). The highest activity is displayed by complexes **3** and **6**, followed by the chelate **1**, with total TONs of 43, 42 and 39 and turnover frequency (TOF) values of 7.2, 7.0 and 6.5 h^{-1} , respectively, for the latter peroxide-to-catalyst ratio. These values are comparable to those we have achieved (maximum TON of 46)^[58] with vanadium catalysts like Amavadin $[\text{V}(\text{O}, \text{N}-\text{L})]^{2-}$ ($\text{O}, \text{N}-\text{L}$ = tribasic form of HIDPA) and $[\text{VO}\{\text{N}(\text{CH}_2\text{CH}_2\text{O})_3\}]$. The other complexes (**2**, **4** and **5**) are less active for sufficiently high H_2O_2 /catalyst ratios, with total TONs (ca. 21–22) that are half of those of the other complexes, for the above peroxide-to-catalyst ratio.



Scheme 2.

Table 2. Peroxidative oxidation of cyclohexane catalyzed by the Re complexes.^[a]

Catalyst	Turnover number (TON) ^[b]		Turnover frequency (TOF) ^[d]
	Cyclohexanol	Cyclohexanone	
1	24	15	6.5
2	13	8	3.5
3 ^[e]	27	16	7.2
4	14	8	3.7
5	13	9	3.7
6 ^[f]	25	17	7.0

[a] Selected data from Table S1. $n(\text{H}_2\text{O}_2)/n(\text{C}_6\text{H}_{12}) = 2:1$, $n(\text{H}_2\text{O}_2)/n(\text{Re catalyst}) = 32000$, molar yield (% relative to substrate) = $6.3 \times \text{TON} \times 10^{-3}$, unless stated otherwise. [b] Mol product/mol Re catalyst precursor. [c] Cyclohexanol + cyclohexanone. [d] Mol products/mol Re catalyst precursor per hour. [e] For $n(\text{H}_2\text{O}_2)/n(\text{C}_6\text{H}_{12}) = 16:1$ the molar yield is 1.9%. [f] For $n(\text{H}_2\text{O}_2)/n(\text{C}_6\text{H}_{12}) = 16:1$ the molar yield is 2.4%.

Higher catalytic activities would be expected upon further increase of the peroxide-to-catalyst ratio (see Figure 7), but this was not tested for safety reasons. All catalysts dis-

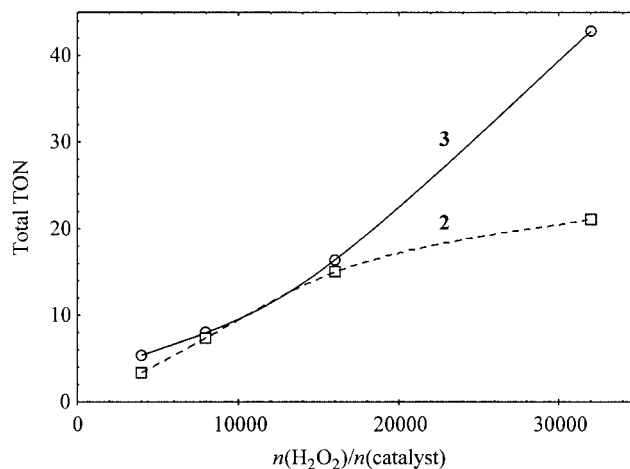


Figure 7. Effect of the oxidant-to-catalyst molar ratio on the total TON values in the oxidation of cyclohexane catalyzed by complexes **2** and **3**.

play a higher selectivity towards the formation of cyclohexanol, in comparison with cyclohexanone, and the average alcohol/ketone molar ratio is within the 1.5–1.8 range.

The Re complexes also catalyze the peroxidative oxidation of cyclopentane to the corresponding cyclopentanol and cyclopentanone, but the catalytic activity (Table S2 in the Supporting Information) is lower than for the oxidation of cyclohexane. The TONs also increase with the amount of hydrogen peroxide. For a peroxide-to-catalyst molar ratio of 32000, the total TON is 13 when using complex **6** as a catalyst, whereas the other complexes exhibit lower TON values (from 3 to 8).

In contrast with the lower activity for cyclopentane than for cyclohexane oxidation, a higher selectivity is observed for the formation of the alcohol, i.e. cyclopentanol, for moderately high peroxide-to-catalyst molar ratios. In fact, cyclopentanol is the only oxidation product detected for all the complexes at $n(\text{H}_2\text{O}_2)/n(\text{catalyst}) = 16000$. However, the formation of cyclopentanone, a more oxidized product, also occurs for complexes **3** and **6** at the higher value of 32000 for the peroxide-to-catalyst molar ratio.

The peroxidative oxidation of cycloalkanes is believed to proceed by a radical mechanism since no traces of cyclohexanol or cyclohexanone are detected when the above reactions that normally lead to the highest TON values are performed in the presence of a radical trap like 2,6-di-*tert*-butyl-4-methylphenol (BHT; 0.5 molar ratio with respect to the alkane). Although we have not yet succeeded in the isolation and full characterization of intermediates, the process conceivably involves^[46,47,50,58,78–80] the formation of intermediate peroxo and oxo complexes. It is noteworthy that the oxo-peroxomethylrhenium(VII) complex $[(\text{Me})\text{ReO}(\text{O}_2)]$ is the active species of the known $[(\text{Me})\text{ReO}_3]/\text{H}_2\text{O}_2$ system in olefin and aromatic oxidations.^[16] Peroxo-derived radical complexes could abstract an H atom from the alkane (RH) to generate an R $\cdot$ radical, which, on reaction with a hydroperoxo or hydroxo complex, could lead to the

alcohol ROH; further oxidation of the latter would yield the corresponding ketone.

The role of the chelating N,O and diazenido ligands in our systems is still unclear but one can postulate their involvement (e.g. upon decoordination, in the former, of a single N or O atom) in proton-transfer steps among oxo-, peroxy- and hydroxo-Re complexes. Such a role in the promotion of proton transfer from coordinated H₂O₂ to oxo ligands has been proposed^[78,79] for some vanadium systems with N,O additives as cocatalysts.

Re-catalyzed alkane oxidations are essentially unexplored. In the only previously published case, the organometallic [(Me)ReO₃]/pyrazine-2-carboxylic acid system was found to be active for the peroxidative oxidation of cyclohexane by anhydrous H₂O₂ in refluxing acetonitrile solution at 80 °C (TON of 126),^[80] however, if aqueous 30% H₂O₂ was used almost no oxidation of cyclohexane occurred.^[80] Our systems have the advantage of operating under milder conditions, i.e. at room temperature, with aqueous H₂O₂ and without added acid. Nevertheless, in all the cases the yields (based on the alkane), under the experimental conditions used, are still modest (not above 3% for our complexes and even lower (1.5%) for [(Me)ReO₃]), although these are still significant in the field of alkane functionalization under mild or moderate conditions. A maximum yield of 9% was achieved^[58] for the same alkane reaction with the above vanadium catalysts.

Conclusions

This work has shown that the benzoylhydrazido chelate [ReCl₂{NNC(O)Ph}(PPh₃)₂] (**1**), which is a recognized key starting material for a diversity of hydrazido, diazenido and even dinitrogen Re complexes with P-based coligands (organophosphanes, -phosphites or -phosphonites), can also provide a convenient entry point for the synthesis of benzoylhydrazido and benzoyldiazenido complexes of Re (in the +5 and the +3 oxidation states) with chelating N,O,O- and N,O-coligands of various types, including amino alkoxides and amino-, oxyamino-, imino- and pyridinocarboxylates. π -Electron delocalization along the hydrazido- and diazenidorhenium moiety has been observed, with the Re–N bond exhibiting some double-bond character. The benzoyldiazenido ligand occupies the *trans* position relative to the O-ligated carboxylato group, preferably to the softer N atom of the N,O- or N,O,O-ligand, an observation that may be of synthetic significance and deserves further exploration.

This study also demonstrates, for the first time, that Re coordination compounds can act as catalysts for alkane hydroxylation and oxygenation, by showing the unprecedented catalytic activity of such a type of complexes, under mild conditions, in the peroxidative oxidation of cycloalkanes to the corresponding alcohols and ketones. The reactions appear to follow a radical mechanism, although complete details have yet to be established. The catalytic activity, although appreciable in the field of mild alkane functionalization, is still modest. Hence, this study provides a

contribution towards the development of the still underdeveloped field of catalysis with rhenium inorganic coordination compounds. However, more-effective systems are needed, as well as the extension to other types of alkane-functionalization reactions, points that are currently being addressed in our laboratory.

Experimental Section

General Materials and Procedures: All synthetic work was performed under nitrogen using standard Schlenk techniques. The solvents were dried over appropriate drying agents and degassed by standard methods. Potassium perchlorate (Merck), triphenylphosphane (Aldrich), benzoylhydrazine (Aldrich), triethanolamine (Fluka), *N,N*-bis(2-hydroxyethyl)glycine (bicine; Aldrich), picolinic acid (Aldrich), 2,6-di-*tert*-butyl-4-methylphenol (BHT; Aldrich), bromoacetic acid (Merck), hydroxylammonium chloride (Aldrich) and zinc acetate (Aldrich) were obtained from commercial sources and used as received. [*N*-Benzoylhydrazido(3-)-*N'*,*O*]dichlorobis-(triphenylphosphane)rhenium(v) [ReCl₂{NNC(O)Ph}(PPh₃)₂] (**1**),^[25,26] *N*-hydroxyiminodiacetic acid^[81] and *N*-hydroxy-2,2'-iminodipropionic acid^[81] were prepared by published methods.

Elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. Melting points were determined on a Kofler 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. 1.18×10^{15} J) Xe atoms. Mass calibration for data system acquisition was achieved with CsI. IR spectra (4000–400 cm⁻¹) were recorded on a Jasco FT/IR-430 instrument as KBr pellets. ¹H and ¹³C{¹H} NMR spectra were measured on a Varian UNITY 300 spectrometer at ambient temperature.

[Re{(OCH₂CH₂)₂N(CH₂CH₂OH)}{NNC(O)Ph}(PPh₃)] (2**):** An excess of triethanolamine (43 μ L, 0.327 mmol) was added to a suspension of **1** (100 mg, 0.109 mmol) in 7.5 mL of MeOH and the reaction mixture was refluxed for about 5 h. The resulting dark-brown clear solution was concentrated under reduced pressure and then treated with 20 mL of Et₂O. The solid (triethanolamine hydrochloride) that separated out from the resulting solution was filtered off and discarded. The filtrate was evaporated under reduced pressure to give a green oil, which was dissolved in 1.5 mL of C₆H₆. The addition of *n*-pentane (20 mL) caused the precipitation of a solid, which was filtered off, washed with *n*-pentane (3 $\times$ 10 mL) and dried in vacuo to yield complex **2** as a green solid. Yield: 43 mg (54% based on **1**). Product **2** is soluble in MeOH, Me₂CO, Et₂O and C₆H₆. M.p. 153 °C (dec.). C₃₁H₃₃N₃O₄PRE (728.79); calcd. C 51.02, H 4.56, N 5.76; found C 50.50, H 4.53, N 5.56. FAB⁺-MS (NBA): *m/z* = 730 [M⁺ + H], 612 [M⁺ – (N₂COPh) + O], 596 [M⁺ – (N₂COPh)], 467 [M⁺ – PPh₃]. FTIR (KBr): $\tilde{\nu}$ = 3416 and 3311 (s br.) ν (OH), 2960 (m) ν_{as} (CH), 2853 (m) ν_s (CH), 1436 (s) ν (NN), 1355 (s) ν (C–O) cm⁻¹. ¹H NMR (CDCl₃): δ = 7.88–7.83 (m, 5 H, Ph), 7.49–7.32 (m, 15 H, PPh₃), 3.66 (t, *J* = 5.4 Hz, 4 H, CH₂-O), 2.69 (t, *J* = 4.8 Hz, 4 H, CH₂-N), 2.37–2.18 (m, 4 H, CH₂CH₂OH) ppm. ¹³C{¹H} NMR (CDCl₃): δ = 134.2, 134.1, 130.0, 129.7, 128.1 and 128.0 (PPh₃), 132.9, 131.6, 130.6 and 127.6 (Ph), 60.3, 58.1, 59.6 and 56.7 (CH₂) ppm; PhCO was not observed. X-ray quality crystals were grown at 5 °C by vapour diffusion of *n*-C₅H₁₂ into an Et₂O or an acetone solution of **2**.

[ReCl{N(CH₂COO)(CH₂CH₂OH)(CH₂CH₂OH)}{N=NC(O)Ph}-(PPh₃)] (3**):** A mixture of **1** (50 mg, 0.055 mmol) and bicine (27 mg, 0.165 mmol) was refluxed in MeOH (10 mL) for about 8 h. The

resulting dark-brown clear solution was concentrated to 5 mL under reduced pressure and 30 mL of Et₂O was added. The obtained greenish-brown solution was left to stand for 2 d at room temperature. During this time greenish-blue microcrystals of **3** separated out of the solution. They were collected, washed with MeOH (3 × 10 mL) and dried in vacuo. Yield: 21 mg (48% based on **1**). Product **3** is slightly soluble in DMSO and insoluble in C₆H₆, MeOH, Me₂CO, CHCl₃ and CH₂Cl₂. M.p. 201 °C (dec.). C₃₁H₃₂ClN₃O₃PRe (779.24): calcd. C 47.78, H 4.14, N 5.39; found C 47.57, H 3.96, N 5.21. FAB⁺-MS (NBA): *m/z* = 744 [M⁺ – Cl], 610 [M⁺ – Cl – (N₂COPh)], 582 [M⁺ – Cl – {N(CH₂CH₂OH)₂ – (CH₂COO)}]. FTIR (KBr): $\tilde{\nu}$ = 3429 and 3265 (s br.) ν (OH), 2925 (m) ν_{as} (CH), 2854 (m) ν_{s} (CH), 1631 (s) ν (C=O), 1458 (s) ν (N=N) cm^{–1}. ¹H NMR (CDCl₃): δ = 7.77–7.33 (m, 20 H, PPh₃ + Ph), 4.25–3.59 and 3.15–2.97 (m, 10 H, CH₂) ppm. ¹³C{¹H} NMR (CDCl₃): δ = 179.1 (PhC=O), 167.6 (CH₂C=O), 134.1, 133.6, 132.9, 131.6, 130.7, 130.3, 129.3, 128.7 and 128.1 (PPh₃ + Ph), 56.0, 55.6, 54.9, 53.6, and 16.2 (CH₂) ppm. X-ray quality crystals of **3**·H₂O were grown by slow evaporation at 5 °C of Et₂O/MeOH or MeOH/Me₂CO solutions.

[ReCl{N(=O)CH₂COO}{N=NC(O)Ph}(PPh₃)₂] (**4**): An excess of HIDA (28 mg, 0.18 mmol) was added to a suspension of **1** (50 mg, 0.055 mmol) in 10 mL of MeOH and the reaction mixture was refluxed for about 7 h. The resulting reddish-yellow clear solution was concentrated under reduced pressure and then treated with 30 mL of Et₂O. The solid that separated out from the resulting solution was filtered off and discarded. The filtrate was evaporated under reduced pressure to give a light-brown oil, which was dissolved in 5 mL of C₆H₆ to form a yellow cloudy solution. Filtration, followed by concentration under reduced pressure, yielded a yellow oil to which 1 mL of benzene was added. The addition of *n*-pentane (20 mL) led to the precipitation of a solid that was filtered off, washed with *n*-pentane (3 × 10 mL) and dried in vacuo to yield complex **4** as a yellow powder. Yield: 19 mg (35% based on **1**). Product **4** is soluble in MeOH, EtOH, Me₂CO, Et₂O, C₆H₆ and CHCl₃. M.p. 220 °C (dec.). C₄₅H₃₇ClN₃O₄P₂Re (967.40): calcd. C 55.84, H 3.83, N 4.34; found C 55.73, H 3.77, N 4.07. FAB⁺-MS (NBA): *m/z* = 966 [M⁺ – H], 879 [M⁺ – (ONCH₂COO)], 832 [M⁺ – (N₂COPh) – 2H], 746 [M⁺ – (ONCH₂COO) – (N₂COPh)]. FTIR (KBr): $\tilde{\nu}$ = 2925 (w) ν_{as} (CH), 1700 (s) ν (C=O), 1626 (s) ν (N=O), 1513 (s) ν (N=N) cm^{–1}. ¹H NMR (CDCl₃): δ = 7.74–7.70 and 7.41–7.43 (m, 30 H, PPh₃), 7.62–7.58 (m, 5 H, Ph), 2.32 (s, 2 H, CH₂) ppm. ¹³C{¹H} NMR (CDCl₃): δ = 195.5 (PhC=O), 174.5 (CH₂C=O), 134.4, 134.3, 130.4, 128.4 and 128.4 (PPh₃), 133.7, 132.4, 128.8 and 127.9 (Ph), 29.0 (CH₂) ppm. X-ray quality crystals were grown by slow evaporation at 5 °C of an EtOH/Me₂CO solution of **4**.

[ReCl{HN=C(Me)COO}{N=NC(O)Ph}(PPh₃)₂] (**5**): Compound **5** was prepared by following the general procedure described for **4**, but using HIDPA instead of HIDA. Yield: 21 mg (40% based on **1**). It is soluble in MeOH, EtOH, Me₂CO, Et₂O, C₆H₆ and CHCl₃. M.p. 114 °C (dec.). C₄₆H₃₉ClN₃O₃P₂Re (965.43): calcd. C 57.20, H 4.07, N 4.35; found C 57.50, H 4.29, N 4.09. FAB⁺-MS (NBA): *m/z* = 967 [M⁺ + 2H], 932 [M⁺ – Cl + 2H], 879 [M⁺ – {HN=C(CH₃)COO}], 834 [M⁺ – (N₂COPh) + 2H], 799 [M⁺ – Cl – (N₂COPh) + 2H], 746 [M⁺ – {HN=C(CH₃)COO} – (N₂COPh)], 711 [Re(PPh₃)₂]. FTIR (KBr): $\tilde{\nu}$ = 3280 (w) ν (N–H), 1656 (s br.) ν (C=O), 1630 (m) ν (C=N), 1436 (s) ν (N=N) cm^{–1}. ¹H NMR (CDCl₃): δ = 7.88–7.84 and 7.17 (m, 5 H, Ph), 7.73–7.32 (m, 30 H, PPh₃), 1.46 (s) + 1.43 (s) (3 H, CH₃) ppm; NH was not observed. ¹³C{¹H} NMR (CDCl₃): δ = 192.4 (PhC=O), 182.2 (N=C(Me)C=O), 134.3, 134.0, 132.2, 132.0, 128.6 and 128.5 (PPh₃), 130.5, 128.9, 128.1, 128.0 and 127.4 (Ph), 51.3 (CH₃) ppm; C=N was not

observed. X-ray quality crystals of **5**·EtOH were grown by slow evaporation at 5 °C of EtOH/C₆H₆ or EtOH/CH₂Cl₂ solutions.

[ReCl{C₅H₄N(COO)}{N=NC(O)Ph}(PPh₃)₂] (**6**): A mixture of **1** (50 mg, 0.055 mmol) and picolinic acid (21 mg, 0.165 mmol) was refluxed in MeOH (10 mL) for about 12 h. The resulting deep-red cloudy solution was taken to dryness under reduced pressure to give a red residue to which 30 mL of MeOH was added to obtain a suspension of **6**. This was filtered off, washed with MeOH (3 × 15 mL) and dried in vacuo to furnish complex **6** as a red solid. Yield: 30 mg (55% based on **1**). Product **6** is soluble in Me₂CO, Et₂O, C₆H₆, CH₂Cl₂ and CHCl₃. M.p. 232 °C (dec.). C₄₉H₃₉ClN₃O₃P₂Re (1001.5): calcd. C 58.73, H 3.93, N 4.20; found C 58.45, H 4.16, N 4.02. FAB⁺-MS (NBA): *m/z* = 1002 [M⁺ + H], 966 [M⁺ – Cl], 868 [M⁺ – (N₂COPh)], 879 [M⁺ – (C₅H₄NCOO)], 833 [M⁺ – Cl – (N₂COPh)], 746 [M⁺ – (C₅H₄NCOO) – (N₂COPh)], 711 [Re(PPh₃)₂], 571 [M⁺ – Cl – (N₂COPh) – PPh₃], 448 [RePPh₃]. FTIR (KBr): $\tilde{\nu}$ = 1673 and 1638 (s) ν (C=O), 1456 (s) ν (N=N), 1307 (m) ν (C–O) cm^{–1}. ¹H NMR (CDCl₃): δ = 7.80–7.73 (m, 4 H, PyH), 7.59–7.43 (m, 30 H, PPh₃), 6.95–6.85 (m, 5 H, Ph) ppm. ¹³C{¹H} NMR (CDCl₃): δ = 134.6, 134.5, 134.2, 133.8, 130.2, 130.0, 128.4, 128.3, 128.0 and 127.8 (PyC, PPh₃ and Ph) ppm; C=O was not observed. X-ray quality crystals of **6**·Me₂CO were grown by slow evaporation at 5 °C of an acetone solution.

Catalytic Studies: The reaction mixtures were prepared as follows: MeCN (3.00 mL), H₂O₂ (30% in H₂O; 10.00 mmol) and cycloalkane (cyclohexane or cyclopentane; 5.00–0.625 mmol) were added, in this order, to 0.313–5.00 × 10^{–3} mmol of the Re complex **1–6** (used either as a solid or as a 0.02 M MeCN solution) in the reaction flask. The reaction mixture was stirred for 6 h at room temperature and normal pressure, then 90 μ L of cycloheptanone (as internal standard) and 10.00 mL of diethyl ether (to extract the substrate and the organic products from the reaction mixture) were added. The obtained mixture was stirred for 10 min and then a sample was taken from the organic phase 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. The obtained results for cyclohexane and cyclopentane oxidation are given as Supporting Information (Tables S1 and S2, respectively); selected values are given in Table 2.

Blank experiments were performed for both cycloalkanes with H₂O₂ and confirmed that no product of alkane oxidation was obtained in the absence of metal catalyst.

X-ray Crystal Structure Determinations: Crystals of **1–5** were immersed in perfluoropolyether, mounted in a cryo-loops and measured at 100 K. The X-ray diffraction data were collected with a Nonius-Kappa CCD diffractometer (for **1–5**) or an Enraf–Nonius MACH3 diffractometer (for **6**), equipped with graphite monochromator and using Mo-K α radiation. The Denzo-Scalepack program package^[82] was used for cell refinements and data reductions for **1–5**. All structures were solved by direct methods using the SIR97 or SIR2002 programs^[83,84] with the WinGX graphical user interface.^[85] An empirical absorption correction was applied to all data (**1–5**) using XPREP in the SHELXTL v.6.12 program^[86] ($T_{\text{min}}/T_{\text{max}}$: 0.21031/0.28346, 0.11746/0.15556, 0.21094/0.26735, 0.12878/0.17642, 0.16825/0.21003 for **1–5**, respectively). All structures were refined with the SHELXL-97 program.^[87] In the structure of **5** C3 and C5 were refined over two positions with occupancies of 0.57 and 0.43 and the position of the OH hydrogen (H98) was estimated with the CALC-OH program.^[88] Other OH, H₂O and NH hydrogens were located from the difference Fourier map. All other hydrogens were placed in idealized positions and constrained to ride on

Table 3. Crystal data for compounds 1–6.

	1·C ₆ H ₆	2	3·H ₂ O	4	5·2 EtOH	6·Me ₂ CO
Empirical formula	C ₄₉ H ₄₁ Cl ₂ N ₂ O ₂ P ₂ Re	C ₃₁ H ₃₃ N ₃ O ₄ PRe	C ₃₁ H ₃₄ ClN ₃ O ₆ PRe	C ₄₅ H ₃₇ ClN ₃ O ₄ P ₂ Re	C ₅₀ H ₅₁ ClN ₃ O ₅ P ₂ Re	C ₅₂ H ₄₅ ClN ₃ O ₄ P ₂ Re
Molecular mass	992.88	728.77	797.23	967.37	1057.53	1059.50
Temp. (K)	100(2)	100(2)	100(2)	100(2)	100(2)	293(2)
λ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073	0.71069
Crystal system	triclinic	monoclinic	triclinic	monoclinic	monoclinic	orthorhombic
Space group	<i>P</i> 1	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 1	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁	<i>Pcab</i>
<i>a</i> [Å]	11.2196(7)	9.783(2)	8.9359(2)	13.8666(6)	11.6355(2)	15.418(2)
<i>b</i> [Å]	11.9274(10)	25.322(5)	11.2862(3)	13.9601(8)	18.0462(5)	19.021(2)
<i>c</i> [Å]	17.6911(12)	11.297(2)	16.0694(5)	20.4390(10)	12.0749(3)	31.593(3)
α [°]	108.027(4)	90	73.7750(10)	90	90	90
β [°]	98.785(4)	91.23(3)	80.903(2)	96.954(3)	112.9970(10)	90
γ [°]	106.011(4)	90	77.423(2)	90	90	90
<i>V</i> [Å ³]	2089.2(3)	2797.9(10)	1510.55(7)	3927.5(3)	2333.94(10)	9265.1(18)
<i>Z</i>	2	4	2	4	2	8
$\rho_{\text{calcd.}}$ [Mg m ^{−3}]	1.578	1.730	1.753	1.636	1.505	1.519
μ (Mo–K α) [mm ^{−1}]	3.153	4.443	4.213	3.292	2.779	2.799
<i>R</i> ₁ ^[a] [<i>I</i> ≥ 2 σ (<i>I</i>)]	0.0379	0.0327	0.0268	0.0463	0.0274	0.0459
<i>wR</i> ₂ ^[b] [<i>I</i> ≥ 2 σ (<i>I</i>)]	0.0765	0.0590	0.0648	0.1010	0.0594	0.0652

[a] $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. [b] $wR_2 = [\Sigma \{w(F_o^2 - F_c^2)^2\} / \Sigma \{w(F_o^2)^2\}]^{1/2}$.

their parent atom. The crystallographic data are summarized in Table 3 and selected bond lengths and angles are given in Table 1. CCDC-256902 to –256907 (for 1·C₆H₆, 2, 3·H₂O, 4, 5·2 EtOH and 6·Me₂CO, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information: Supplementary tables with the TON values for the peroxidative oxidation of cyclohexane (Table S1) and cyclopentane (Table S2) catalyzed by the Re complexes 1–6 (see also footnote on first page of this article).

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