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New η^5- and μ-(O)-Rh(I) phenoxide complexes: synthesis, characterisation and unconventional reactivity of η^5-complexes towards carbon dioxide

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Abstract

The synthesis, analytical and spectroscopic characterisation, and reactivity of three new Rh(I)–phenoxide complexes of formula $Rh_2(\mu\text{-}OPh)_2(C_2H_4)_4$ (**1**), $Rh(C_2H_4)_2(\eta^5\text{-}OPh)$ (**2**) and $Rh(diphos)(\eta^5\text{-}OPh)$ (**4**) [diphos = 1,2-bis(diphenylphosphino)ethane] are reported. Both the η^5- and μ-(O) modes of bonding have been found. The η^5-complexes are quite air-sensitive. The reactivity towards carbon dioxide is described and the formation of an emicarbonate is reported with the O-bonded phenoxide. A ring carboxylation occurs with η^5-complexes. © 2000 Published by Elsevier Science S.A. All rights reserved.

Keywords: Phenoxides; Phenoxo-complexes; Rhodium complexes; Carbon dioxide; Carboxylation

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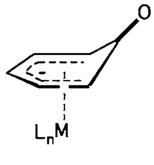
1. Introduction

Recently, the chemistry of alkoxo-[1] and aryloxo-complexes [1a,e,2] of transition metals has been investigated in detail with the aim of collecting information on the reactivity of the metal–oxygen bond [3], considering the potential of these compounds in synthetic chemistry [4–6] and in the catalytic conversion of alcohols [1d]. A particular interest lies with the utilisation of these compounds in the synthesis of oxalates and organic carbonates, in alcohol oxidation, and in carbo–alkoxylation-, carboxylation- and carbo-imidation reactions [7]. As part of our studies on the formation of C–C, C–O, C–N bonds via carbon dioxide fixation [8,9], we have synthesised new Rh (this paper) and Mn [10] complexes with the phenoxide anion as a ligand, in order to investigate the correlation mode of bonding-reactivity.

It is known that phenoxide ion can coordinate to a metal centre through either the O-atom (σ-bond) or the phenyl-ring electron-system (π-bond). The former coordination mode is expected for acid metal centres or for metal centres bearing strong donor ligands. In this case, the phenoxo-ligand can behave as a terminal- or a bridging-ligand. Electron rich metal centres and strongly unsaturated metal systems (10 or 12 e^- systems) seem to prefer the π-coordination mode, usually described as η^5-OPh (see A), as it involves the *ortho*, *meta* and *para* carbon atoms of the aromatic ring. The *ipso* carbon lies far away from the metal atom. According to this mode of bonding, the planarity of the phenoxo ring is practically lost with consequent reduction of its aromatic character and the π-bonded anion can be more properly described as a η^5-cyclohexadienonyl ligand. Ru [11], Rh [11a,12] and rare examples of Cr [13] and Mn [14] π-complexes have been reported until now. Very interestingly, only one mode of bonding has been found per each metal system.



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Moreover, the reaction of M–O bonds with carbon dioxide [15] has been studied for its relevance to the synthesis of organic carbonates and transition metal emicarbonates are well documented. Conversely, the reactivity of η^5-phenoxo complexes towards CO_2 has never been described. We have found that the mode of bonding of the phenoxo-ligand to the metal can drive the reaction with carbon dioxide in the direction of insertion into the M–O bond or towards the ring-carboxylation [10].

In this paper we present an interesting example of O-σ and ring-π bonding of the phenoxide anion to the $(C_2H_4)_2Rh$ moiety, the characterisation of Rh(diphos)(η^5-OPh) [diphos = 1,2-bis(diphenylphosphino)ethane] via ^1H- and ^{13}C-NMR in various solvents and the reaction with carbon dioxide of the Rh-complexes so obtained. The η^5-Rh complexes reported in this paper are rare examples of isolated and fully characterised in the solid state (elemental analysis, IR) and solution (NMR) covalent compounds having the unsubstituted phenoxo-ring coordinated to the metal without further bonding to free phenol via H-bonding.

2. Results and discussion

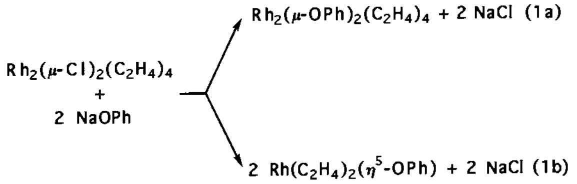
2.1. Synthesis and characterisation of the Rh-complexes $Rh_2(\mu\text{-}OPh)_2(C_2H_4)_4$ (**1**) and $Rh(C_2H_4)_2(\eta^5\text{-}OPh)$ (**2**)

The reaction of $Rh_2(\mu\text{-}Cl)_2(C_2H_4)_4$ with NaOPh in rigorously anhydrous benzene under a dinitrogen atmosphere at 283 K affords an apparently orange solid, not conducting in nitrobenzene, analysing correctly for $Rh(OPh)(C_2H_4)_2$. The determination of the molecular mass (by crioscopy [16]) in benzene gives the value of 465, somewhat lower than the value of 504, calculated for the dimer $Rh_2(\mu\text{-}OPh)_2(C_2H_4)_4$ (**1**) in which phenoxide would act as O-bonded ligand bridging the two Rh-atoms. This mode of bonding is also supported by the IR spectrum that shows characteristic bands at 1228, ν(C–O), and 429 cm^{-1}, ν(Rh–O). The band at 1228 cm^{-1} is in the range usually reported for the stretching of the single bond C–O in phenoxo-anions O-bonded to metal atoms [3c,d,11a,12a,17–20]. The presence of a band of medium intensity at 1576 cm^{-1}, that cannot be simply attributed to the C=C double bond stretching, coupled with the molecular mass determination data, suggests that the compound is not the pure dimer. In fact, the IR band is in the range where the ν(C=O) of π-bonded phenoxide is found [11a,12,13].

The ^1H-NMR (200 MHz, 293 K) spectrum of the material in CD_2Cl_2 shows, besides the very broad ethylene resonance at 2.20, intense signals at 7.15 (m, H_{meta}) and 6.84 ppm (m, H_{ortho} and H_{para}). The two last signals are found in the usual range for the protons of a phenoxo-anion σ-bonded to a metal [2d,3d,12b,18–22]. Besides the previous ones, low intensity signals at 4.88, 5.75 and 6.29 ppm are evident. These resonances are in the range that is usual for π-bonded phenoxo-complexes [11a,12a,b,e,13,23,24].

The ^{13}C-NMR (50.3 MHz, 293 K) spectrum in $CDCl_3$ clearly shows two sets of peaks of quite different intensity. The first group is formed by the lines at 157.45 (s, C_{ipso}), 128.32 (s, C_{meta}), 123.45 (s, C_{ortho}), 120.77 (s, C_{para}) of the phenoxo-ligand and at 56.99 ppm (d, $^1J(Rh\text{–}C) = 14.9$ Hz, $C_{ethylene}$) that can be attributed to the O-bonded dimer form [2a–c,20,25]. The second group of signals is formed by the resonances at 105.6 (d, $^1J(Rh\text{–}C) = 3.6$ Hz), 98.6 (d, $^1J(Rh\text{–}C) = 2.4$ Hz), 83.7 (d, $^1J(Rh\text{–}C) = 2.2$ Hz), assigned to the *ortho*, *meta* and *para* carbon atoms of the phenoxo ligand, and at 49.3 ppm (d, $^1J(Rh\text{–}C) = 12.3$ Hz, $C_{ethylene}$). The signal of the *ipso* phenoxo–carbon is not visible in the spectrum. The existence of a coupling of the phenoxo–carbon atoms with Rh, that is not found in the first set of signals, clearly indicates that the second group of resonances cannot be related to an O-bonded species, but most likely is due to a phenoxide anion coordinated to Rh through the phenyl ring electrons: $Rh(C_2H_4)_2(\eta^5\text{-}OPh)$ (**2**). However, our NMR data are in good agreement with the data available in the literature for such metal systems [11c,d,12c,e].

These figures suggest that the material obtained by reaction of $Rh_2(\mu\text{-}Cl)_2(C_2H_4)_4$ with NaOPh is indeed a mixture of two complexes, one bearing the phenoxide anion O-bonded to Rh, the other with the phenoxo-group π-bonded (Eq. (1)a and b). The two species having similar solubility in several organic solvents were separated after a long fractional crystallisation procedure. The two quite pure compounds have each the set of the spectroscopic properties discussed above. The molecular mass (determined by crioscopy) for the dimer is 495. The monomer shows a molecular mass of 240. This is the first case for which it has been demonstrated the existence of the two forms of bonding of phenoxide anion to the same metal system. We have not observed any interconversion process of the pure compounds in solution. Moreover, despite several trials, we were not able to set preparative conditions selective for one of the two species. The most abundant compound is always the O-bonded complex (90–98%). The reaction solvent is not selective neither, if non-coordinating and non-protic solvents are used.



We have also attempted the synthesis of the phenoxo–ethylene complex starting from $Rh(C_2H_4)_2(O_3SCF_3)$, produced in situ by reaction of $Rh_2(\mu\text{-}Cl)_2(C_2H_4)_4$ with silver triflate in THF (see Section 4). Also in this case the product is essentially formed by **1** (> 98%), as demonstrated by the ^1H- and ^{13}C-NMR analysis.

2.2. Synthesis and characterisation of Rh(diphos)(η^5-OPh) (**4**)

The reaction of Rh(diphos)Cl [26], prepared in situ from the Cramer's complex and diphos (Eq. (2)), with NaOPh in benzene, under

$$Rh_2(\mu\text{-}Cl)_2(C_2H_4)_4 + \text{diphos} \xrightarrow{C_6H_6} 2Rh(\text{diphos})Cl + 4C_2H_4 \quad (2)$$

pure dinitrogen, affords, after crystallisation from benzene–pentane, two products: a brown material, **3** and an orange solid, **4** that analyses correctly for Rh(diphos)(η^5-OPh) (Eq. (3)).

$$Rh(\text{diphos})Cl + NaOPh \xrightarrow{C_6H_6} Rh(\text{diphos})(\eta^5\text{-}OPh) + NaCl \quad (3)$$

Compound **3** appears to be a mixture of compounds and contains chlorinated species and the oxide of the diphos ligand. Its formation is still under investigation, as the operative conditions exclude in this case, as for all other syntheses, the presence or entrance of air or moisture in the reaction vessel. Compound **4** is a monomeric complex (molecular mass determined by crioscopy in benzene: Found 585, Calc. 594), extremely sensitive to dioxygen and moisture in solution. Complex **4** shows in the IR spectrum in Nujol a strong band at 1588 cm^{-1} attributed to the stretching of the C–O bond of the phenoxo-ligand. The position of this band suggests π-coordination of phenoxide anion. Two bands at 1264 and 1247 cm^{-1} are attributed to the deformation of the group C–C(O)–C that has a partial ketone character. These bands are present in the spectrum of the NaOPh at 1321 and 1299 cm^{-1} and are shifted upon coordination.

Table 1
^{31}P NMR data for $Rh^I(L\text{–}L)$ and $Rh^I(L\text{–}L)_2$ complexes

Complex	Solvent	δ_P (ppm)	^1J(P–Rh) (Hz)	Reference
Rh(diphos)(η^5-OPh)	C_6D_6	72.07	200.2	This work
Rh(diphos)(Ph)	$CDCl_3$	74.6	199.1	[27]
$Rh_2(\mu\text{-}Cl)_2(\text{diphos})_2$	CD_2Cl_2	71.8	198.4	[27]
[Rh(diphos)$(CH_3CN)_2$]Cl	THF	74.65	176	[27]
Rh(diphos)(η^6-BPh_4)	THF	74.28	206	[27]
[Rh(diphos)$_2$]Cl	CD_2Cl_2	59.4	133.5	[28]
$Rh_2(\mu\text{-}Cl)_2(\text{dppp})_2$ [a]	$(CH_3)_2CO$	30.3	184	[28]
[Rh(dppp)$_2$]Cl [a]	CD_2Cl_2	6.4	132	[28]

[a] dppp is 1,2-bis(diphenylphosphino)propane.

The NMR data unambiguously confirm the structure of the complex in solution and support the coordination of phenoxide through the phenyl ring electrons.

The $^{31}P\{^1H\}$-NMR (81 MHz, C_6D_6, 293 K) spectrum presents a single signal at 72.07 ppm, $^1J(P\text{–}Rh) = 200.2$ Hz, characteristic of Rh-complexes bearing one diphos ligand coordinated to the metal centre (see Table 1) [27,28]. The inspection of the data reported in Table 1 shows that both the position of the resonance and the value of the P–Rh coupling constant are useful diagnostic tools for deciding if one or two chelating phosphorus ligands are bonded to Rh. Moreover, while the position of the P-resonance depends strongly on the magnitude (five or six) of the P–Rh–P ring (see the δ value for the analogous diphos and dppp complexes in Table 1), the value of ^1J(P–Rh) is much more independent from this parameter and more closely related to the number of chelating ligands coordinated to Rh and the coordination number of Rh.

The ^1H and ^{13}C spectra of the phenoxo-group of **4** show inequivocally, the coordination through the phenyl ring electron-system. This mode of bonding is clearly supported by (a) the fact that the ^1H and ^{13}C signals of the π-phenoxo-ligand are upfield shifted with respect to the positions where they are usually found in systems containing a phenoxo group σ-O-bonded to the metal; (b) the splitting of the π-phenoxo-ligand ^{13}C resonances upon coupling with Rh and/or P. Such couplings are not found when the phenoxo-ligands are σ-O-bonded to L_nRh (L may be a P ligand) moieties. However, their presence in the ^{13}C spectrum results to be a useful diagnostic tool for supporting the π-coordination of the phenoxo-ligand.

Complex **4** has been characterised by NMR spectroscopy in different solvents (Table 2). Interestingly, the multiplicity of the π-phenoxo-bonded ^{13}C resonances seems to be affected by the nature of the solvent. As a matter of fact, in C_6D_6 (unlike CD_2Cl_2), they appear as singlets, likewise what reported, in the same solvent (C_6D_6), for $(Ph_3P)_2Rh(\pi\text{-}OPh)\cdot 2PhOH$ [12f], known for a long time [11a] and structurally characterised recently in the solid state [12f].

Moreover, also the position of the resonances of the π-phenoxide is dependent on the solvent used (Table 2). In chlorinated solvents ($CDCl_3$ and CD_2Cl_2), an upfield shift of the proton resonances with respect to benzene is observed. As from Table 2, the observed shifts are: $\Delta_{ortho} = 1.08$ ($CDCl_3$) and 1.42 (CD_2Cl_2), $\Delta_{meta} = 1.23$ ($CDCl_3$) and 0.70 (CD_2Cl_2), $\Delta_{para} = 2.02$ ppm ($CDCl_3$) and 1.55 (CD_2Cl_2). The most evident difference is relevant to the *para* proton. We can exclude that benzene coordinates to Rh or displaces the phenate anion. In fact, no signals that can be assigned to free phenoxide can be observed in the ^1H and ^{13}C

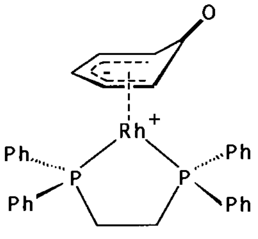
Table 2
Solvent dependence of ^1H- and ^{13}C-NMR phenoxide resonances (in ppm) for Rh(diphos)(η^5-OPh) [a]

Solvent	H_{ortho}	H_{meta}	H_{para}
C_6D_6 [b]	7.13 dd $J = 8.5$ and 1	6.69 dd $J = 8.5$ and 7.1	6.45 tt $J = 7.1$ and 1
CD_2Cl_2 [c]	5.71 d $J = 6.8$	5.99 t $J = 6.4$	4.90 t $J = 6.5$
$CDCl_3$ [b]	6.05 d [d] $J \cong 7$	5.46 dd $J = 7.2$ and 5.6	4.43 t [d] $J \cong 6$
Solvent	C_{ortho}, C_{meta}, C_{para}		$C_{ipso,OPh}$
C_6D_6 [e]	115.87 s, 114.41 s, 100.19 s		168.43 s
CD_2Cl_2 [e]	115.74 d,102.80 dd, 96.32 m		162.0 s

[a] J values are in Hz.
[b] At 200 MHz.
[c] At 500 MHz.
[d] Each term of the signal shows further poorly resolved minor splittings.
[e] At 50.3 MHz.

spectra of **4** in C_6D_6. Moreover, the ^{13}C spectrum of **4** in C_6D_6 does not show any resonance that can be attributed to a C_6D_6 ring π-coordinated to a Rh(diphos) moiety.

A similar solvent dependence has been documented previously by us for the proton resonances of the BPh_4^- phenyl ring η^6-coordinated to the Rh(diphos) moiety in Rh(diphos)(η^6-$PhBPh_3$) [27]. This effect may be the result of particular interactions between the metal complex and the solvent molecules in the outer coordination sphere and, in the case of **4**, could reflect a different degree of distortion from planarity of the π-coordinated phenoxo-ring in solution, depending on the nature of solvent. The higher up-field proton shifts observed in $CDCl_3$ and CD_2Cl_2 with respect to C_6D_6 may suggest a greater distortion of the phenoxo-structure towards a cyclohexanedienone system (see B) in chlorinated solvents and, consequently, a more marked deviation from planarity than in benzene.



(B)

Complex **4**, in solution, is very air sensitive: the phenoxide is readily converted into catechole. This is the first evidence for such phenoxide–catecholate conversion upon the oxidation of the π-coordinated phenoxide anion. The amount of phenoxide oxidised depends on the reaction conditions. Studies are in progress in order to shed light on this aspect.

Complexes **2** and **4** are the first examples of covalent Rh compounds bearing the unsubstituted phenoxide anion π-coordinated to the metal without a further binding, through hydrogen bonding, to a phenol molecule. In fact, the two other classes of Rh-complexes well characterised were either cationic complexes bearing the unsubstituted phenoxide π-coordinated to Rh [12e] or complexes of formula $RhL_2(OAr)$ where Ar is the bulky (2,6-*ter*-Bu-4-Me-C_6H_2O) group that gives a special stability to the π-bonded complex [12c].

2.3. Reaction of the phenoxo-complexes with carbon dioxide

We have studied the reactivity of complexes **1**, **2**, **4** with carbon dioxide, in order to understand if the coordination of the phenoxide can induce a different reactivity. In principle, the π-cordination stabilises a keto-form with a delocalisation of a negative charge on the aromatic ring. This could change the reactivity towards CO_2, as the nucleophilic centre is at one of the phenyl-carbons, more than at the oxygen atom.

Complex **1** does not react with carbon dioxide (0.1 MPa) in the solid state, while, in $CHCl_3$ solution, it slowly (24 h) affords a brown powder, **5** whose IR spectrum shows bands at 1531 and 1343 cm^{-1} characteristic of organic emicarbonate moieties bonded to metal centres [29]. Ethylene is not lost during the reaction, as demonstrated by the IR bands at 1210, 991, 904, 829 and 731 cm^{-1} present in the final product. These results infer that carbon dioxide interacts preferably with the Rh–O bond to afford a carbonate complex more than with the coordinated ethylene to afford the formation of a metallacarboxylate [30,31] or acrylate species [32]. Such situation is also supported by the ^{13}C-NMR spectrum of the analogous complex **5a** obtained by reaction of **1** with $^{13}CO_2$, that shows a resonance at 165.47 ppm, not present in the spectrum of the parent compound. This signal is a doublet (J(CRh) = 2.8 Hz) and is attributed to the carbonate carbon of **5a** [33,34]. The value is in the range usually found for the metal carbonate complexes (155–170 ppm) [6,29a].

The reaction of **5** with HCl affords the starting $Rh_2(\mu\text{-}Cl)_2(C_2H_4)_4$ complex and emicarbonic acid PhOC(O)OH that rapidly converts into CO2 and phenol also in the presence BF_3–MeOH [35].

Complexes **2** and **4**, that bear a π-bonded phenoxide, react with carbon dioxide in a different way. Indeed, the emicarbonate is not produced and a new complex is formed that bears a ring-functionalised phenoxide. As a matter of facts, treatment of **6**, obtained by reaction of **4** with CO_2, with dry HCl produces 4-OH-benzoic acid dosed by HPLC or, after treatment with CH_3OH–BF_3, by GC–MS as the methyl ester. These data suggest that the carboxylation takes place at the ring, as we have observed for analogous π-bonded-phenate Mn-complexes [10]. This reaction is a unique example of direct ring carboxylation of phenol at room temperature (r.t.) and pressure. The delocalisation of the negative charge from the oxygen atom, in free phenoxide, to the phenyl ring, in π-coordinated phenoxide, makes the latter enough nucleophilic to react with CO_2 and afford 4-OH-benzoic acid more than emicarbonates. It is worth to emphasise that the carboxylation takes place very selectively at the four-position (100% selectivity). Salicilic acid is not observed. This reaction is reminiscent of the benzene electro-carboxylation upon coordination to Cr(0) and electron transfer to the coordinated ring via electrochemical reduction [36]. Also in this case, the enhanced nucleophilicity of the ring-carbon atoms makes benzene enough reactive to afford benzoic acid.

3. Conclusions

This study reports on the synthesis and characterisation of three novel covalent Rh(I)–phenoxide complexes, **1**, **2** and **4**, and their reactivity towards carbon dioxide.

Complexes **1** and **2** are formed simultaneously, but with different yields, by reaction of $Rh_2(\mu\text{-}Cl)_2(C_2H_4)_4$ with NaOPh in benzene. They represent the first documented example in which phenoxide anion exhibits two different coordination modes towards the same metal centre, $Rh(C_2H_4)_2$.

Complex **4** is very air sensitive and has been obtained by an analogous synthetic procedure, by reacting Rh(diphos)Cl with NaOPh in benzene and full characterised by elemental analysis and NMR spectroscopy in several solvents.

Complexes **2** and **4** are rare examples of covalent π-phenoxo–Rh-complexes in which the π-coordination of the aryloxo ligand to the metal is not further stabilised by hydrogen bonding with free phenol molecules.

We have also shown that the coordination mode of phenoxide to Rh affects the reactivity of the coordinated ligand towards carbon dioxide and controls the regioselectivity of the attack by the heterocumulene. In fact, O-bonded phenoxide in complex **1** reacts with the heterocumulene at the oxygen atom in a conventional way to give the Rh–carbonate complex **5**. Conversely, in complexes **2** and **4**, in which the negative charge is displaced from the O-atom of phenoxide to the ring, the electrophilic attack by CO_2 is addressed onto the π-bonded aromatic ring, resulting in the selective carboxylation of the π-phenoxide in *para* position to afford 4-OH-benzoic acid.

4. Experimental

4.1. General procedures

Unless otherwise specified all manipulations were made under dinitrogen using the vacuum-line technique. Solvents were purified by standard methods [37]. $Rh_2(\mu\text{-}Cl)_2(C_2H_4)_4$, diphos, silver triflate, phenol, potassium and sodium were commercial products (Aldrich). CO_2 (99.995%) and $^{13}CO_2$ (^{13}C 99%) were from Air Liquide and CIL, respectively.

IR spectra were obtained with a Perkin–Elmer 883 spectrophotometer. ^1H-, ^{31}P- and ^{13}C-NMR spectra were recorded with a Varian XL-200 or a Bruker AM 250 or 500. Proton and carbon chemical shifts are in ppm versus TMS and have been referenced to the solvent peak, while ^{31}P resonances were calibrated with respect to 85% H_3PO_4. Electrolytic conductivity measurements were made on a WTW conductivity meter apparatus. Molecular weights were determined by cryoscopy using the apparatus described in Ref. [16]. GC–MS analyses were carried out with a HP 5890 gas-chromatograph linked to a HP 5970 selective mass detector (capillary column: 30 m SE-30, 0.25 mm ID, 0.25 μm film thickness). Gas analysis was performed with a Carlo Erba Fractovap Mod. C Instrument or a DANI 86.10 GC with a TC detector, using a Chromosorb or 4 Å molecular sieves packed column. HPLC analyses were made using a Perkin–Elmer Series 4 LC connected with a LC290 UV–vis spectrophotometric detector.

4.2. Synthesis of sodium phenoxide and potassium phenoxide

To a cold (273 K) solution of phenol (7.52 g, 79.9 mmol) in diethyl ether (150 ml) sodium (1.67 g, 76.2 mmol) powder was added. The reaction mixture was stirred at r.t. (293 K) until complete reaction of the metal (about 20 h). The white solid precipitated was filtered out, washed with diethylether (30 ml) and dried in vacuo. Yield: 7.24 g, 86% versus sodium. Anal. Found: C, 62.00; H, 4.30. Calc. for C_6H_5ONa: C, 62.07; H, 4.34%. IR (Nujol): 3061 m, 1584 vs (br), 1479 vs, 1321 s, 1299 s, 1166 s, 986 s, 871 s, 823 s, 764 s, 700 s cm^{-1}. ^1H-NMR (250 MHz, CD_3CN, 293 K): δ 6.23 (tt, $^3J_{H_{para}-H_{meta}} = 7.12$ Hz, $^4J_{H_{para}-H_{ortho}} = 1$ Hz, H_{para}), 6.40 (m, H_{ortho}), 6.93 (m, H_{meta}). $^{13}C\{^1H\}$-NMR (50.3 MHz, CD_3CN, 293 K): δ 111.1 (s, C_{para}), 119.5 (s, C_{ortho}), 129.2 (s, C_{meta}), 170.3 (s, C_{ipso}).

Potassium phenoxide was prepared in a similar way and isolated in 90% yield. Anal. Found: C, 54.47; H, 3.85. Calc. for C_6H_5OK: C, 54.51; H, 3.81%. IR (Nujol): 3057 m, 1584 s, 1546 m, 1474 s, 1314 s, 1304 s, 1250 m, 1161 m, 1145 m-w, 1064 m-w, 1014 m-w, 985 m, 980 m, 878 m, 820 m, 790 m, 782 m, 761 m, 718 m, 711 m, 700 m, 534 m, 450 m cm^{-1}.

4.2.1. Reaction of $Rh_2(\mu\text{-}Cl)_2(C_2H_4)_4$ with NaOPh

NaOPh (0.207 g, 1.78 mmol) in THF (3 ml) was added dropwise, under a dinitrogen stream, to a filtered, cold (283 K) solution of $Rh_2(\mu\text{-}Cl)_2(C_2H_4)_4$ (0.347 g, 0.892 mmol) in benzene (75 ml). The solution colour changed from yellow–orange to pale yellow. The reaction mixture was stirred at 283 K for 24 h. The formed NaCl was filtered off and the mother solution concentrated in vacuo to 10 ml. Pentane (40 ml) was layered on the benzene solution and the system cooled to 253 K. After 24 h a yellow–orange solid formed that was filtered, washed with pentane and dried in vacuo. The solid is soluble in benzene, toluene, CH_2Cl_2, $CHCl_3$ and THF. Yield: 73% versus Rh. Spectroscopic analyses show that the solid is a mixture of two products: $Rh_2(\mu\text{-}OPh)_2(C_2H_4)_4$ (**1**) and $Rh(C_2H_4)_2(\eta^5\text{-}OPh)$ (**2**), that have the same elemental analysis. Anal. Found: C, 47.86; H, 5.41. Calc. for $C_{10}H_{13}ORh$: C, 47.64; H, 5.20%. The two complexes were separated by repeated crystallisation from benzene–pentane. Complex **1** is slightly less soluble than complex **2**.

4.2.2. Spectroscopic characterisation of $Rh(\mu\text{-}OPh)_2(C_2H_4)_4$ (1)

Anal. Found: C, 47.71; H, 5.35. Calc. for $C_{10}H_{13}ORh$: C, 47.64; H, 5.20%. ^1H-NMR (200 MHz, CD_2Cl_2, 293 K): δ 2.20 (very broad, $H_{ethylene}$), 6.78–6.90 (m, H_{ortho} and H_{para}), 7.15 (m, H_{meta}). $^{13}C\{^1H\}$-NMR (50.3 MHz, $CDCl_3$, 293 K): δ 56.99 (d, $^1J(Rh–C) = 14.9$ Hz, $C_{ethylene}$), 120.77(s, C_{para}), 123.45 (s, C_{ortho}), 128.32 (s, C_{meta}), 157.45 (s, C_{ipso}).

4.2.3. Spectroscopic characterisation of $Rh(C_2H_4)_2(\eta^5\text{-}OPh)$ (2)

Anal. Found: C, 47.80; H, 5.40. Calc. for $C_{10}H_{13}ORh$: C, 47.64; H, 5.20%. ^1H-NMR (200 MHz, CD_2Cl_2, 293 K): δ 2.20 (broad, $H_{ethylene}$), 4.88, 5.75 and 6.29 (multiplets assigned to the aromatic protons). $^{13}C\{^1H\}$-NMR: (50.3 MHz, $CDCl_3$, 293 K): δ 49.3 (d, $^1J(Rh–C) = 12.3$ Hz, $C_{ethylene}$), 83.7 (d, $^1J(Rh–C) = 2.2$ Hz), 98.6 (d, $^1J(Rh–C) = 2.4$ Hz), 105.6 (d, $^1J(Rh–C) = 3.6$ Hz) (*ortho*, *meta* and *para* carbon atoms of π-OPh).

4.2.4. Reaction of $Rh(C_2H_4)_2(O_3SCF_3)$ with KOPh

Silver triflate (0.36595 g, 1.46 mmol) in THF (20 ml) was added dropwise, under a dinitrogen stream, to a filtered, cold (263 K) solution of $Rh_2(\mu\text{-}Cl)_2(C_2H_4)_4$ (0.30415 g, 0.704 mmol) in THF (20 ml). After stirring for 30 min, the reaction mixture was filtered out to remove the AgCl precipitated. To the mother solution, containing $Rh(C_2H_4)_2(O_3SCF_3)$ prepared in situ [38], a solution of KOPh (0.20220 g, 1.53 mmol) in 15 ml of THF was added. The reaction mixture was stirred at 273 K for 3 h, concentrated in vacuo to 15 ml and filtered. Upon addition of pentane (30 ml) and cooling to 253 K, a yellow–orange solid precipitated that was isolated by filtration. The spectroscopic features (^1H-, ^{13}C-NMR) of this material show that the isolated product is still a mixture of **1** (> 98%) and **2**.

4.3. Synthesis of $Rh(diphos)(\eta^5\text{-}OPh)$ (4)

To a filtered solution of $Rh_2(\mu\text{-}Cl)_2(C_2H_4)_4$ (0.306 g, 0.787 mmol) in benzene (100 ml) the phosphine (0.628 g, 1.57 mmol) in 15 ml of benzene was added dropwise, under dinitrogen and with vigorous stirring. A yellow solid formed that redissolved under stirring. Evolved ethylene was eliminated under vacuum. To the clear solution of Rh(diphos)Cl, NaOPh (0.183 g, 1.57 mmol), dissolved in THF (3 ml), was added dropwise. The solution was stirred for 24 h and then filtered. The solid (NaCl) was washed with benzene (3 × 5 ml) and discharged. The mother solution was concentrated in vacuo to 10 ml and 50 ml of pentane were added. By slow diffusion of pentane a brown solid **3** was formed that was filtered. By cooling the resulting solution to 253 K an orange solid **4** separated that was isolated by filtration and dried in vacuo. Yield: 60%. Anal. Found: C, 64.44; H, 4.87; P, 10.39. Calc. for $C_{32}H_{29}P_2ORh$: C, 64.66; H, 4.92; P, 10.42%. Complex **4** is very air sensitive, soluble in benzene, $CHCl_3$, CH_2Cl_2. The formation of **4** is very solvent dependent. If the reaction is carried out in toluene or CH_2Cl_2, **4** was not formed.

Solid **3** is a mixture of compounds and has the following elemental analysis. Found: C, 56.94; H, 4.51; P, 8.68; Cl, 2.15%. The IR spectrum shows the presence P=O groups. This is quite peculiar as air was totally excluded during the reaction. This solid is still under investigation.

4.3.1. Spectroscopic characterisation of $(diphos)Rh(\eta^5\text{-}OPh)$ (4)

IR (Nujol): 3053 m, 1588 s ν(C=O), 1478 vs, 1432 s (sharp), 1264 s, 1247 s, 1157 m, 1100 m, 1067 m-w, 1020 m-w, 996 m, 878 m, 847 m, 817 m-s, 740 m-s, 696 s, 689 s, 534 s, 493 s, 425 m cm^{-1}. ^1H-NMR (200 MHz, C_6D_6, 293 K): δ 1.67 (d, $J = 17.28$ Hz, $CH_2–CH_2$), 6.45 (tt, $^3J_{H_{para}–H_{meta}} = 7.1$ Hz, $^4J_{H_{para}–H_{ortho}} = 1$ Hz, $H_{para,OPh}$), 6.69 (dd, $^3J_{H_{meta}–H_{ortho}} = 8.5$ Hz, $H_{meta,OPh}$), 7.13 (dd, $H_{ortho,OPh}$), 6.9–7.1, 8.02–8.14 (multiplets assigned to the aromatic protons of diphos). Assignments and evaluation of the coupling constants for the π-phenoxo protons were supported by decoupling experiments. ^1H-NMR (500 MHz, CD_2Cl_2, 293 K): δ 2.15 (dd, $J = 20$ and 1.2 Hz, $CH_2–CH_2$), 4.90 (t, $J = 6.5$ Hz, $H_{para,OPh}$), 5.99 (t, $J = 6.4$ Hz, $H_{meta,OPh}$), 5.71 (d, $J = 6.8$ Hz, $H_{ortho,OPh}$), 7.38–7.42, 7.60–7.65 (multiplets assigned to the aromatic protons of diphos). $^{13}C\{^1H\}$-NMR (50.3 MHz, C_6D_6, 293 K): δ 28.15 (m, $CH_2–CH_2$), 100.19 (s, C_{OPh}), 114.41 (s, C_{OPh}), 115.87 (s, C_{OPh}), 128.04 (virtual t, $J = 4.6$ Hz, $C_{meta,diphos}$), 129.70

(s, $C_{para,diphos}$), 133.95 (virtual t, $J = 5.6$ Hz, $C_{ortho,diphos}$), 136.56 (virtual t, $J = 19.1$ Hz, $C_{ipso,diphos}$), 168.43 (s, $C_{ipso,OPh}$). $^{13}C\{^1H\}$-NMR (50.3 MHz, CD_2Cl_2, 293 K): δ 29.2 (m, CH_2–CH_2), 96.32 (m, C_{OPh}), 102.80 (dd, $J = 2.3$ and 3.8 Hz, C_{OPh}), 115.74 (d, $J = 3.3$ Hz, C_{OPh}), 128.23 (virtual t, $J = 5.0$ Hz, $C_{meta,diphos}$), 129.79 (s, $C_{para,diphos}$), 132.09 (virtual t, $J = 6.1$ Hz, $C_{ortho,diphos}$), 137.87 (virtual t, $J = 20.3$ Hz, $C_{ipso,diphos}$), 162.0 (s, $C_{ipso,OPh}$). $^{31}P\{^1H\}$-NMR (81 MHz, C_6D_6, 293 K): δ 72.07 (d, $J_{P-Rh} = 200.2$ Hz).

*4.4. Reaction of $Rh_2(\mu\text{-}OPh)_2(C_2H_4)_4$ (**1**) with CO_2*

$Rh_2(\mu\text{-}OPh)_2(C_2H_4)_4$ (**1**) (0.150 g) was dissolved in 3 ml of $CHCl_3$ under carbon dioxide and the solution was stirred for 24 h. A brown solid **5** separates that was filtered off and dried in vacuo. The brown solid is not soluble in aromatic and halogenated solvents but is soluble in DMSO. IR (Nujol) 1531 m ν(C=O), 1343 m-w cm^{-1}. $^{13}C\{^1H\}$-NMR (50.3 MHz, DMSO-d_6, 293 K): δ 165.47 (d, J(Rh–C) = 2.8 Hz).

When complex **5** is treated with HCl, PhOH and carbon dioxide (confirmed by GC) were produced, confirming the nature of emicarbonate of **5**.

*4.5. Reaction of Rh(diphos)(η^5-OPh) (**4**) with CO_2*

Complex **4** (0.05 g) was dissolved in 3 ml of CD_2Cl_2–CH_2Cl_2 (1:2, v/v) and reacted in a NMR tube for 24 h with $^{13}CO_2$. The clear solution showed new signals at 115.3 (s), 119.7 (s), 134.6 (s), 156.6 (s), and 165.3 ppm (d, J(Rh–C) = 8.4 Hz), while the resonances at 96.3, 102.8 and 115.7 ppm, due to the π-bonded phenoxide, disappeared. The new signals and specifically the intense one at 165.3 ppm, suggests that CO_2 has reacted with the Rh-complex to afford a new species, **6** containing fixed CO_2. The exact nature of this Rh-carboxylated compound could not be clarified in detail, as the attempts to isolate it in a pure form were unsuccessful. However, it bears a phenoxo-group carboxylated in *para* position, as demonstrated by the acidolysis experiments with HCl.

The above solution was reacted with dry HCl and then analysed by HPLC using the following conditions:

- column: Erbasil C18/M, 25 × 0.46 cm;
- mobile phase: acetonitrile (20%, v/v)/phosphate buffer (80%, v/v; pH 3.5) containing 0.1% (v/v) of butanol;
- flow: 1 ml min^{-1}

The HPLC analysis of the reaction solution showed the presence of 4-OH-benzoic acid.

The acidified solution was evaporated in vacuo and the residue was treated with 0.5 ml of methanol and 0.6 ml of BF_3–OEt_2. The mixture was heated at 333 K, then treated with 1 ml of water, and extracted with 1 ml of 1:1 diethyl ether–pentane (v/v). The analysis of the organic phase by GC–MS using a SE-30 capillary column showed the presence of 4-OH-benzoic acid methyl ester.

The body of these results clearly demonstrates that upon reaction of **4** with carbon dioxide, the π-bonded phenoxo-ligand is selectively carboxylated in *para* position.

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