

Available online at www.sciencedirect.com



Polyhedron 27 (2008) 530-536

POLYHEDRON www.elsevier.com/locate/poly

# A general route for the synthesis of hydrido-carboxylate complexes of the type $MH(CO)(\kappa^3-OCOR)(PPh_3)_2$ [M = Ru, Os; R = CH<sub>3</sub>, CH<sub>2</sub>Cl, C<sub>6</sub>H<sub>5</sub>, CH(CH<sub>3</sub>)<sub>2</sub>] and their use as precatalysts for hydrogenation and hydroformylation reactions

Merlín Rosales <sup>a,\*</sup>, Beatriz Alvarado <sup>a</sup>, Federico Arrieta <sup>b</sup>, Carlos De La Cruz <sup>c</sup>, Ángel González <sup>a</sup>, Karely Molina <sup>a</sup>, Otto Soto <sup>a</sup>, Yslamar Salazar <sup>a</sup>

<sup>a</sup> La Universidad del Zulia (L.U.Z.), Facultad Experimental de Ciencias, Departamento de Química, Laboratorio de Química Inorgánica, Maracaibo, Venezuela

<sup>b</sup> Laboratorio de Química Inorgánica Teorica, Maracaibo, Venezuela <sup>c</sup> Laboratorio de Espectroscopía Molecular y Atómica, Maracaibo, Venezuela

> Received 28 April 2007; accepted 4 October 2007 Available online 26 November 2007

#### Abstract

The synthesis and solid-state IR, <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopic characterization of complexes of the type MH(CO)( $\kappa^3$ -OCOR)-(PPh<sub>3</sub>)<sub>2</sub> [M = Ru, Os; R = CH<sub>3</sub>, CH<sub>2</sub>Cl, C<sub>6</sub>H<sub>5</sub> and CH(CH<sub>3</sub>)<sub>2</sub>] are reported in this paper. These compounds were obtained by reaction of the respective cationic complex [MH(CO)(NCMe)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>]BF<sub>4</sub> with the sodium salt of the corresponding carboxylic acid in a 1:1 v/v dichloromethane/methanol solution at room temperature. The spectroscopic data of these complexes and some DFT calculations reveal an octahedral geometry with a bidentated carboxylate, two equivalent triphenylphosphines in a mutually *trans* positions, a linear hydride and a linear carbonyl both in the *cis*-positions of the coordination sphere. The catalytic results indicate that these complexes are efficient and regioselective precatalysts for the quinoline hydrogenation and for the hydroformylation of 1-hexene, under mild reaction conditions (130 °C and 4 atm H<sub>2</sub> and 120 °C and 15 atm H<sub>2</sub>/CO, respectively). For benzothiophene hydrogenation, the osmium complexes showed low activities whereas the analogous ruthenium complexes were catalytically inactive under somewhat more drastic reaction conditions to those of the quinoline hydrogenation (140 °C and 10 atm H<sub>2</sub>).

© 2007 Elsevier Ltd. All rights reserved.

Keywords: Ruthenium; Osmium; Carboxylate; Quinoline; Benzothiophene; Hydrogenation; 1-Hexene; Hydroformylation

# 1. Introduction

The chemistry of ruthenium and osmium complexes containing hydrido, carbonyl and trivalent phosphorus coligands has attracted continuous attention because of the wide variety of structures and reactivities exhibited by these

\* Corresponding author. Fax: +58 261 7598125.

E-mail address: merlin2002@cantv.net (M. Rosales).

compounds [1,2]. Perhaps the Vaska and Diluzio's complex RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub> [3] is the most thoroughly studied compound of this series [2]. Interaction of this compound, or alternatively of RuH<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>3</sub>, with carboxylic acids produces RuCl( $\kappa^3$ -OCOR)(CO)(PPh<sub>3</sub>)<sub>2</sub> and RuH( $\kappa^3$ -OCOR)(CO)(PPh<sub>3</sub>)<sub>2</sub>, where R = CH<sub>3</sub> [4,5], C<sub>2</sub>H<sub>5</sub>, C<sub>6</sub>H<sub>5</sub> [4], C(CH<sub>3</sub>)<sub>3</sub>, C<sub>6</sub>H<sub>11</sub>, CH<sub>2</sub>Cl, CF<sub>2</sub>Cl, CF<sub>3</sub> [5]. Examples of analogous osmium-complexes are rather scarce in the literature [6] and, to our knowledge, complexes of the type OsH( $\kappa^3$ -OCOR)(CO)(PPh<sub>3</sub>)<sub>2</sub> have not been synthesized.

<sup>0277-5387/\$ -</sup> see front matter @ 2007 Elsevier Ltd. All rights reserved. doi:10.1016/j.poly.2007.10.007

Furthermore, interest in hydrido-carboxylate complexes of transition-metals have been further enhanced by their catalytic activity in a number of industrially important chemical reactions [7].

In the present paper, we reported the synthesis and spectroscopic characterization of a group of complexes with general formulae  $MH(\kappa^3 \text{-}OCOR)(CO)(PPh_3)_2$  [M = Ru and Os; R = CH<sub>3</sub>, CH<sub>2</sub>Cl, C<sub>6</sub>H<sub>5</sub> and CH(CH<sub>3</sub>)<sub>2</sub>]; these were tested as precatalysts for the homogeneous hydrogenation of polynuclear heteroaromatic nitrogen and sulfur compounds (quinoline and benzothiophene) and for the olefin hydroformylation (1-hexene).

#### 2. Results and discussion

# 2.1. Synthesis and characterization of complexes $MH(CO)(\kappa^3 - OCOR)(PPh_3)_2$

The complexes  $MH(CO)(\kappa^3-OCOR)(PPh_3)_2$  (III–X) were synthesized in high yields (>70%) by reaction of the respective cationic complex [MH(NCMe)<sub>2</sub>(CO)(PPh\_3)<sub>2</sub>]-BF<sub>4</sub> (Ru = I and Os = II) with the sodium salt of the corresponding carboxylic acid in a 1:1 v/v dichloromethane/ methanol solution, at room temperature (see Eq. (1)).



The products III-X were white unstable solids that had to be manipulated and stored strictly under N2 atmosphere. Three of the hydrido-carboxylate ruthenium complexes ( $R = CH_3$ ,  $CH_2Cl$  and  $C_6H_5$ ) were reported early by Dobson and Robinson [4] by the reaction of RuH<sub>2</sub>-(CO)(PPh<sub>3</sub>)<sub>3</sub> with the corresponding carboxylic acid and by Sánchez-Delgado et al. [5] by slight modifications of the Robinson's method. However, this method is not of general use for Ru complexes, in the sense that the reaction time, the amount of the carboxylic acid added and the solvent used depend of the carboxylate ligand. On the other hand, the synthetic route that we are reporting in this article is of general application and allowed us to prepare the osmium analogues which, to our knowledge, were unknown to the date. No satisfactory analytical data could be obtained for these complexes, which darken after a few hours even under inert atmosphere at room temperature. Structural characterization of these complexes had to be based on their FT-IR and NMR spectroscopic properties and by comparison of those with the spectra from wellknown complexes.

The FT-IR spectra of all complexes III–X showed medium-to-weak absorptions between 2150 and 2000 cm<sup>-1</sup>, and very strong and broad bands between 1900 and 1950 cm<sup>-1</sup>. Comparison with the reported data for RuH- $(CO)(\kappa^3 - OCOCMe_3)(PPh_3)_2^1$  and  $OsHCl(CO)(PPh_3)_3$  [8]<sup>2</sup> allowed us to assign the main bands in these wavenumber regions to the v(MH) and v(CO) vibrations of terminal MH and linear MCO groups, respectively [9]. The C–O distance is estimated to be  $1.15 \pm 0.02$  Å for the carbonyls of these complexes [9b]. The wide wavenumber range found for the v(MH) vibration relative to the v(CO)-range shows the high sensitivity of the metal-hydrogen bond to changes in electron density around the central metal atom [9b]. This is affected by the type of metal in question [i.e. v(RuH) = $2010-2070 \text{ cm}^{-1}$  whereas  $v(\text{OsH}) = 2090-2133 \text{ cm}^{-1}$  and by charge donation or withdrawal of the other co-ligands [e.g. v(RuH) = 2019 or  $2036 \text{ cm}^{-1}$  for  $RuH(CO)(\kappa^3$ - $OCOCH_3)(PPh_3)_2$  or  $RuH(CO)(\kappa^3-OCOCH_2Cl)(PPh_3)_2$ , respectively].

The infrared spectra of the new complexes (with the exception of the Os-complex **VII**) also show the two expected, symmetry-allowed, infrared-active absorptions of the carboxylate group at 1560–1521 [ $v_{asym}(OCO)$ ] and 1457–1425 [ $v_{sym}(OCO)$ ] cm<sup>-1</sup>. These values indicate bidentated coordination between the two equivalent oxygen atoms of the OCOR groups and the Ru or Os atom. Indeed when the carboxyl group is monodentated, one of the C–O bonds should have enhanced double bond character and therefore give rise to a high frequency band in the 1590–1650 cm<sup>-1</sup>-region which is not observed in our spectra [10].

High field <sup>1</sup>H NMR spectra showed triplets between -16.3 and -16.9 ppm with coupling constants close to 20 Hz for the ruthenium complexes, whereas for the corresponding osmium ones the triplets appear between -19.3 and -20.0 ppm (<sup>2</sup>J<sub>HP</sub> close to 16 Hz). These values are consistent with a hydride ligand coupled to two equivalent triplenylphosphines in mutually *trans* positions [5]. This is further supported by the spectra from the <sup>31</sup>P{<sup>1</sup>H}NMR experiments which show singlets between 41.8 and 46.4 ppm and between 23.3 and 25.2 ppm for the Ru and Os compounds, respectively.

Our results and interpretations are summarized in Table 1. It clearly indicates an octahedral geometry with four monodentated ligands (hydride, carbonyl and two  $PPh_3$ ) and one bidentated carboxylate group coordinated to the central Ru or Os atom.

A more detailed analysis of the infrared spectra in the 2100–1850 cm<sup>-1</sup> region (Fig. 1) indicates the presence of two isomers for the above octahedral complexes in solid state, as may be observed by the presence of two hydride bands. For complexes with the general formula RuH(CO)- $(\kappa^3$ -OCOR)(PPh<sub>3</sub>)<sub>2</sub>, four geometrical isomers could be drawn, which are shown in Fig. 2; for convenience we refer to these below as the *trans*-PPh<sub>3</sub>/*trans*-PPh<sub>3</sub> (**A**), *trans*-CO/*trans*-PPh<sub>3</sub> (**B**), *trans*-H/*trans*-PPh<sub>3</sub> (**C**) and *trans*-H/*trans*-CO (**D**) isomers.

<sup>2</sup> For OsHCl(CO)(PPh<sub>3</sub>)<sub>3</sub>. IR: v(Os-H) = 2097 and v(CO) = 1912 cm<sup>-1</sup>.

<sup>&</sup>lt;sup>1</sup> For RuH(CO)(OCO(CH<sub>3</sub>)<sub>3</sub>)(PPh<sub>3</sub>)<sub>2</sub>; IR:  $v(Ru-H) = 2000 \text{ cm}^{-1}$  and  $v(CO) = 1925 \text{ cm}^{-1}$ .

Table 1

532

Selected FT-IRS, <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR data for  $[MH(\eta^3-OCOR)(CO)(PPh_3)_2]$  {M = Ru and R = CH<sub>3</sub> (V), CH<sub>2</sub>Cl (VI), CH(CH<sub>3</sub>) (VII), Ph (VIII); M = Os and R = CH<sub>3</sub> (IX), CH<sub>2</sub>Cl (X) CH(CH<sub>3</sub>)<sub>2</sub> (XI) and Ph (XII)}

Complex	$\frac{\text{FT-IRS}}{\text{Wavenumbers (cm}^{-1}) \text{ and relative intensities}^{c}}$			<sup>1</sup> H NMR <sup>a</sup> Chemical shifts (ppm) and coupling constants (Hz) <sup>d</sup>			$^{31}P{}^{1}H} NMR^{b}$	
								v(MH)
	Ш	2019 (m)	1929 (vs)	1531 (s)	1457 (s)	1.7 (s)	-16.7 (t)	20
IV	2036 (m)	1933 (vs)	1560 (s, br)	1432 (s, br)	2.4 (s)	-16.9 (t)	20	42.8 (s)
V	2070 (sh)	1909 (vs)	1523 (s)	1425 (s)	1.2 (sept) 0.1 (d, $J = 7.1$ )	-16.3 (t)	21	41.8 (s)
VI	2010 (m)	1925 (vs)	1521 (s)	1425 (s)	7.6 (m)	-16.4 (t)	20	46.0 (s)
VII	2110 (br)	1928 (s)	Obscured by	other bands	1.7 (s)	-19.6 (t)	16	24.7 (s)
VIII <sup>e</sup>	2133 (m)	1925 (vs)	1550 (s, br)	1432 (s)	2.0 (s)	-20.0 (t)	16	25.2 (s)
IX	2090 (sh)	1909 (vs)	1556 (s)	1433 (s, br)	1.1 (sept) 0.1 (d, $J = 6.3$ )	-19.3 (t)	17	23.3 (s)
X	2105 (m)	1915 (vs)	1551 (s)	1431 (s)	7.1 (m)	-19.5 (t)	16	24.2 (s)

<sup>a</sup> Negative values are upfield from the signal of external SiMe<sub>4</sub>.

<sup>b</sup> Positive values are downfield from the signal of external 85%  $H_3PO_4$ .

<sup>c</sup> FT-IRS abbreviations: v = bond-stretching, vs = very strong, s = strong, m = medium, w = weak, vw = very weak, br = broad and sh = shoulder.

<sup>d</sup> NMR abbreviations: s = singlet, d = doublet, t = triplet, sept = septuplet, m = multiplet.

<sup>e</sup> The infrared spectrum also shows bands at 3480 (s, br), 2200 (vw, br), 2050 (vw, br), 1910 (s, br), 1610 (vs), 1490 (m), 1410 (s), 1380 (s), 1325 (m) and 1100 (vs) cm<sup>-1</sup>. These can be assigned to vibrational modes of water, N=C M–H, C=O, P–Ph<sub>3</sub> and BF<sub>4</sub><sup>-</sup>. They indicate a mixture of small amounts of [OsH(NCMe)<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub>]BF<sub>4</sub> and OsH(OCOCH<sub>2</sub>Cl)(CO)(PPh<sub>3</sub>)<sub>2</sub> (VIII) which probably adsorbed water during the pressing-disc procedure.

T-1-1- 0



Fig. 1. Possible isomers for complexes  $MH(CO)(\kappa^3-OCOR)(PPh_3)_2$  (M = Ru, Os).

In other to determine the stability of these isomers, theoretical DFT-calculations were performer for these four isomers with the FeH(CO)(OOCH)(PH<sub>3</sub>)<sub>2</sub> models using the STO/6-31+G(d,p) extended basis; in Table 2 are listed the calculated energies of these four isomers. As may be observed the isomer A, which present the two phosphine ligands in a mutually trans position was the more stable isomer, having an energy 20.1, 12.0 and 24.4 kJ mol<sup>-1</sup> lesser than those of **B**, **C** and **D**, respectively. Isomers **B** and **D** were the least stable of the four isomers. The order of stability was  $A \le C \le B \le D$ . In view of these results, we proposed that, in solid state, isomer A was the major isomer whereas C was the minor one. Halide complexes of the type  $MX(CO)(\kappa^3-OCOR)(PPh_3)_2$  have been found to have similar structure to that of A (M = Ru, X = Cl) or C (M = Os,X = Br) isomers.



Fig. 2. FTIR for complexes  $RuH(CO)(\kappa^3-OCOR)(PPh_3)_2$  in the 2100–1850 cm<sup>-1</sup> region.

Optimized total energies (hartrees) of the isomers of the model compoun	d
Fe(H)(CO)(OOCH)(PH <sub>3</sub> ) <sub>2</sub>	

Isomer	Energy
A	-2253.089846
В	-2253.082210
С	-2253.085265
D	-2253.080594

Although small amounts of the isomer C of complexes III–X can be presented (less than 10%) in the solid state, the spectroscopic data in solution are in agreement with a stereochemistry in which the two triphenylphosphine are in a mutually *trans* position, the carboxylate ligand is bonded in a bidentated fashion and the hydride and the carbonyl ligand occupy the *cis* positions of the coordination sphere (isomer A).

# 2.2. Catalytic activities of complexes MH(CO) $(\kappa^3 - OCOR)(PPh_3)_2$

The new Rh and Os complexes  $MH(CO)(\kappa^3-OCOR)(PPh_3)_2$  were tested as catalytic homogeneous precursors for the regioselective hydrogenation of quinoline (Q) to 1,2,3,4-tetrahydroquinoline (THQ) and of benzothiophene (BT) to 2,3-dihydrobenzothiophene (DHBT) under mild temperatures and low hydrogen pressures; see Eqs. (2) and (3).

$$+2 H_2 \xrightarrow{\text{cat}} (2)$$

$$+ H_2 \xrightarrow{\text{cat}} (3)$$

The hydrogenation of the heterocyclic ring of polynuclear heteroaromatic nitrogen and sulfur compounds is an area of considerable interest in connection with the industrially important hydrodenitrogenation (HDN) and hydrodesulfurization (HDS) reactions, respectively [11]. Although some Rh- and Ir-complexes have been used for the hydrogenation of the heterocyclic ring of Q and related compounds, the only ruthenium and osmium precatalysts used in this reaction were RuHCl(PPh<sub>3</sub>)<sub>3</sub> [12], [MH(CO)- $(NCMe)_2(PPh_3)_2]^+$  (M = Ru or Os) [13] and RuCl<sub>2</sub>-(NCMe)<sub>4</sub>/tris(pyrazolyl)borate [14]. Recently, Borowski et al. [15] reported the regioselective hydrogenation of the non-heterocyclic rings of Q, by using  $[RuH_2-(\eta^2-H_2)_2 (PCy_3)_2$  (Cy = cyclohexyl) as the precatalyst. For the BT hydrogenation, the complexes  $[Ru(NCMe)_3(triphos)]^{+2}$ [16] and  $[RuH_2(\eta^2-H_2)_2(PCy_3)_2]$  [17] were the only precursors that showed very high activities for this reaction.

The hydrogenation of Q to THQ was achieved by all of the ruthenium and osmium hydrido-carboxylate complexes with high catalytic activities; the results are collected in Table 3 together with the  $pK_a$  values of the R groups of the carboxylate ligand of the Ru and Os complexes. As may be observed, the ruthenium complexes were twice more active than the corresponding osmium ones. It is clear that the hydrogenation activities of these compounds (except for the hydrido-isobutyrate cases where steric effects seem to be important) are affected by the electronreleasing character of the carboxylate substituents. Thus, for example, a plot of  $\log r_i$  versus  $pK_a$  of the acid from which the carboxylate ligand is derived shows an excellent correlation  $[\log r_i(\text{Ru}) = -6.48 + 0.09 \text{pK}_a, r^2 = 0.99]$ , as may be observed in Fig. 3; for the osmium complexes, a similar tend was observed  $\lceil \log r_i(Os) = -7.17 + 0.17 pK_a$ ,  $r^2 = 0.99$ ]. Sánchez-Delgado et al. [7] found the contrary effect for the propionaldehyde hydrogenation, which was explained through a mechanism involving equilibrium between species containing the carboxylate ligand coordinated in a bi- and monodentated mode. In our case, we

Table 3	
Quinoline hydrogenation catalyzed by MH(CO)(k <sup>3</sup> -OCOR)(PPh <sub>3</sub> )	2

R	$pK_{a}^{a}$	$10^7 r_i ({\rm ms}^{-1})$		
		Ru	Os	
CH <sub>2</sub> Cl	2.86	$6.13\pm0.12$	$2.05\pm0.06$	
C <sub>5</sub> H <sub>6</sub>	4.20	$6.94\pm0.15$	$3.51\pm0.08$	
CH <sub>3</sub>	4.76	$9.24\pm0.09$	$4.23\pm0.08$	
CH(CH <sub>3</sub> ) <sub>2</sub>	4.86	$8.00\pm0.05$	$2.65\pm0.05$	

Conditions:  $[cat] = 1.0 \times 10^{-3} \text{ M}$ , [Q] = 0.17 M,  $p(H_2) = 4 \text{ atm}$ , T = 130 °C, solvent = xylene,  $r_i$  (initial rate) are expressed in means ± SEM; P = 0.05.

 $^a$   $pK_a$  of the acid from which the carboxylate ligand is derived. Yield: 70–80% for Ru complexes and 40–50% for Os ones.

propose that the equilibrium between these two species (Eq. (4)) is very fast and, therefore, is not the rate-determining step of the catalytic reaction. Preliminary kinetic studies indicate that the hydrogenation rate is independent of the amount of quinoline present in the reaction mixture; these results are consistent with the opening of the carboxylate ligand and the coordination of Q molecule being a very fast step.



On the other hand, the hydrogenation of BT to DHBT was observed only with the osmium hydrido-carboxylate complexes (Table 4), the activities being very low (less than 10% conversion); the analogous ruthenium complexes were catalytically inactive for this reaction. Because of the close and very small activities of these osmium systems, no conclusions may be extracted on the relation between activity and the donor character of the carboxylate substituent.



Fig. 3. Hydrogenation of quinoline catalyzed by RuH(CO)- $(\kappa^3$ -OCOR)(PPh<sub>3</sub>)<sub>2</sub> showing the relation between initial rate ( $r_i$ ) and the nature of the carboxylate ligand. Conditions as in Table 3.

In order to find new and lesser expensive precatalysts than the rhodium ones for the alkene hydroformylation, in the present work we used the hydrido-carboxylate complexes MH(CO)( $\kappa^3$ -OCOR)(PPh\_3)\_2 as catalyst precursors for this reaction. This reaction is a well-known synthetic tool for a wide range of organic molecules of commercial value and it is also one of the largest scale applications of homogeneous catalysis in industry. The major capacity is based on the processes using phosphine-modified cobalt [18] and rhodium carbonyl systems [19] but some ruthenium precatalysts have been used for this reaction, such as RuH<sub>2</sub>(CO)<sub>2</sub>(PPh\_3)<sub>2</sub> [20], [RuH(CO)(NCMe)<sub>2</sub>(PPh\_3)<sub>2</sub>]-BF<sub>4</sub> [21], [Ru(CO)<sub>2</sub>( $\eta^5$ -Cp)]<sub>2</sub> [22] and RuH<sub>2</sub>(CO)<sub>2</sub>(TPP-MS)<sub>2</sub> [23].

The ruthenium and osmium hydrido-carboxylate complexes were efficient and regioselective precatalysts for the hydroformylation of 1-hexene towards heptanal and 2methyl-hexanal (Eq. (5)), under mild reaction conditions (120 °C and 15 atm H<sub>2</sub>/CO) in toluene as the solvent; the results in turnover frequency (TF) are showed in Table 5.



The ruthenium complexes were more active than the corresponding osmium ones and similar to the Q hydrogenation described before, the complexes with carboxylates presenting donor groups were more active than those containing electron-withdrawing substituents. Again, this effect may be explained through a mechanism which did not involve the opening of the carboxylate ligand as the rate-determining step. For the ruthenium complexes, a plot of log TF versus  $pK_a$  of the acid from which the carboxylate ligand is derived shows a very good correlation,  $\log \text{TF}(\text{Ru}) = 0.61 + 0.32 \text{pK}_{\text{a}}$ ,  $r^2 = 0.96$  (Fig. 4); a similar graph may be constructed for the osmium analogues  $[\log TF(Ru) = 0.41 + 0.20pK_a, r^2 = 0.92]$ . Finally, the regioselectivity find for ruthenium complexes, measured as the linear to branch ratio (1/b), is ranging between 2.5 and 3.5, which is somewhat higher that those found for other ruthenium complexes; the l/b ratio for the osmium analogues varied from 0.8 to 1.6.

Table 4

Benzothiophene hydrogenation catalyzed by  $OsH(CO)(\kappa^3-OCOR)(PPh_3)_2$ 

R	Conversion (%)	
CH <sub>2</sub> Cl	8.9	
C <sub>5</sub> H <sub>6</sub>	6.2	
CH <sub>3</sub>	8.7	
$CH(CH_3)_2$	9.1	

Conditions:  $[cat] = 1.0 \times 10^{-3} \text{ M}, [BT] = 0.1 \text{ M}, p(H_2) = 15 \text{ atm}, T = 140 \text{ °C}, t = 8 \text{ h}, \text{ solvent} = xylene.$ 

Table 5
Hydroformylation of hex-1-ene catalyzed by MH(CO)(x <sup>3</sup> -OCOR)(PPh <sub>3</sub> )
(M = Ru, Os)

(,)				
R	$pK_a^a$	TF (1/b)		
		Ru	Os	
CH <sub>2</sub> Cl	2.86	38 (2.8)	10 (1.6)	
C <sub>5</sub> H <sub>6</sub>	4.20	80 (3.5)	15 (0.8)	
CH <sub>3</sub>	4.76	155 (2.5)	22 (1.2)	
$CH(CH_3)_2$	4.86	180 (3.0)	27 (0.9)	
	2			

*Conditions*:  $[cat] = 3.3 \times 10^{-3}$  M, [1-hexene] = 1 M,  $p(H_2) = 15$  atm, T = 120 °C, solvent = toluene, TF = mole of product per mole of catalyst per hour, l/b = linear to isoaldehyde ratio.

<sup>a</sup>  $pK_a$  of the acid from which the carboxylate ligand is derived.

The results found both for the Q and BT hydrogenation reactions as for the 1-hexene hydroformylation are promising for two reasons. First, although the Ru precatalysts synthesized in this work are close to one magnitude order less active than Rh ones, ruthenium is a metal less expensive than rhodium and, on the other hand, it is possible through the variation of the electronic properties of the carboxylate and phosphine ligands to increase the catalytic activities of our systems. Finally, it is convenient to mention that Fe complexes have shown to have less catalytic activity for both reactions. For example,  $Fe(CO)_5$  is inactive for quinoline hydrogenation and Fe(CO)<sub>4</sub>(PBu<sub>3</sub>) presented low activity (1% in 5 h) for hydrogenation of 5,6-benzoquinoline under drastic water-gas shift reaction conditions [27], whereas the activities of the Fe systems for olefin hydroformylation are four magnitude order lower than those of the ruthenium ones [18c].

More detailed kinetic and coordination chemistry studies of these catalytic reactions (hydrogenation of Q and BT and olefin hydroformylation) are in progress, aimed at better understanding these systems and at improving even more both the activity as the selectivity properties of the hydroformylation reaction.



Fig. 4. Hydroformylation of 1-hexene catalyzed by RuH(CO)- $(\kappa^3$ -OCOR)(PPh\_3)\_2 showing the relation between turnover frequency (TF) and the nature of the carboxylate ligand. Conditions as in Table 5.

### 3. Experimental

#### 3.1. General considerations

All manipulations were performed under argon using standard Schlenck techniques. Solvents,  $MCl_3 \cdot 3H_2O$ (M = Ru, Os) for the home-made preparation of  $[MH(NCMe)_2(CO)(PPh_3)_2]BF_4$ , M = Ru (I) [21] and Os (II) [13c], quinoline, benzothiophene and 1-hexene were obtained as high purity compounds from Aldrich. Prior to use solvents, quinoline and 1-hexene were distilled over appropriate standard agents under nitrogen. Research grade H<sub>2</sub> and CO gases were obtained from Praxair Venezuela. Before use, these gases were dried by passing them through a column containing CaSO<sub>4</sub>.

#### 3.2. Analytical procedures

FT-IR spectra of dried discs (i.e. solid samples + KBr) were obtained using a 13-mm-die, 13-mm disk holder, a Caver hydraulic press (>12 ton), a vacuum pump and a Shimadzu FTIR-8300 interferometer. High resolution <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectra of the samples dissolved in CDCl<sub>3</sub>were obtained at 300 MHz and 121 MHz, respectively, in a Bruker AC-300 instrument at room temperature; <sup>1</sup>H- and <sup>31</sup>P-chemical shifts are expressed in part per million down-field and up-field from SiMe<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub>, respectively.

Gas chromatographic analyses were performed in a 3300 Series VARIAN instrument fitted with a flame ionization detector (FID) and a 2 m 20% SP-2100 on a 0.1% carbowax 100/120 Supelcoport column, using N<sub>2</sub> as carrier gas and naphthalene (for the Q and BT hydrogenation) and *n*-heptane (for hydroformylation of 1-hexene) as internal standards. The results were quantified with a VARIAN 4400 microcomputer.

#### 3.3. Synthesis of complexes

RuH( $\kappa^3$ -OCOR)(CO)(PPh<sub>3</sub>)<sub>2</sub> [R = CH<sub>3</sub> (III), CH<sub>2</sub>Cl (IV), CH(CH<sub>3</sub>)<sub>2</sub> (V), and Ph (VI)] were prepared by the following method. To a solution of [RuH(NCMe)<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub>]BF<sub>4</sub> (I) (0.5 mmol) in a 1:1 v/v mixture of CHCl<sub>2</sub> and MeOH (25 mL) was added the corresponding carboxylic Na salt (1.5 mmol). The mixture was stirred vigorously at room temperature for 3–4 h, giving a pale yellow solution which was evaporated under vacuum to about, one-third of its initial volume, obtaining a white precipitate. This solid was washed with methanol and diethylether, and then dried in vacuum. It affords white solids (yields: 70–80%).

The corresponding  $OsH(\kappa^3-OCOR)(CO)(PPh_3)_2$  complexes [where  $R = CH_3$  (VII),  $CH(CH_3)_2$  (IX), Ph (X)] were synthesized by a similar method but with a reaction time of approximately 7 h. All products were white solids (yields: 70–80%). However, reaction of [OsH(NCMe)\_2-(CO)(PPh\_3)\_2]BF\_4 (II) with Na[OCOCH\_2Cl] afforded a amourphous, white solid which darken after few minutes

even in inert atmosphere. The infrared spectrum of this solid as KBr pellet revealed a solid mixture of small amounts of compound II and  $OsH(OCOCH_2Cl)-(CO)(PPh_3)_2$  (VIII) (see footnote e of Table 1). So increasing amounts of the Na salt and a longer period of reaction time (8 h) were needed to obtain white microcrystals of complex VIII. <sup>1</sup>H- and proton-decoupled <sup>31</sup>P NMR spectra indicated that only compound VIII was present in the CDCl<sub>3</sub> solutions.

## 3.4. Computational details

The optimized energy calculations of complexes MH- $(\kappa^3$ -OCOR)(CO)(PPh<sub>3</sub>)<sub>2</sub> were carried out using Fe as metal, R = H and the simplified PH<sub>3</sub> analogues in order to have a better calculation level. These were performed with the GAUSSIAN-98 computational package by using the B3LYP [24] hybrid method of density functional density theory (DFT); the optimizations were carried out with the 6-31+G(d,p) basis sets [25].

#### 3.5. Details of the catalytic runs

The apparatus and the reaction procedure for the catalytic runs of hydrogenation [13] and hydroformylation reactions [26] have been described in details elsewhere. Briefly, a solution of the precatalyst, substrate, internal standard and solvent were placed in a high pressure reactor which was flushed three times with argon. When this system reached thermal equilibrium, H<sub>2</sub> (or an H<sub>2</sub>/CO mixture) was admitted into the reactor at the desired pressure. The reactions were followed by both measuring the gas pressure-drop as a function of time and by gas chromatography. Each reaction was repeated at least twice in order to ensure reproducibility of the results. All straight lines were fitted by conventional linear regression programs to  $r^2 > 0.98$ .

#### Acknowledgements

This work was supported from Consejo de Desarrollo Científico y Humanístico through Project (CONDES-0174-02) and for the acquisition of a gas chromatograph. We thank Dr. José Ortega for his valuable help to record the NMR spectra.

#### References

 (a) C.A. McAuliffe (Ed.), Transition Metal Complexes of Phosphorus, Arsenic and Antimony Ligands, MacMillan, London, 1973, pp. 72–86;

(b) C.A. McAuliffe, W. Levanson (Eds.), Phosphine, Arsine and Stibine Complexes of the Transition Elements, Elsevier, Amsterdam, 1979, pp. 112–126.

- [2] R.A. Sánchez-Delgado, M. Rosales, Trends Inorg. Chem. 3 (1993) 479.
- [3] L. Vaska, J.W. Diluzio, J. Am. Chem. Soc. 83 (1961) 1262.
- [4] (a) A. Dobson, S.D. Robinson, Platinum Met. Rev. 20 (1976) 36;
   (b) A. Dobson, S.D. Robinson, Inorg. Chem. 16 (1977) 321.

- [5] R.A. Sánchez-Delgado, U. Thewalt, N. Valencia, A. Andriollo, R.-L. Márquez-Silva, J. Puga, H. Schöllhorn, H.-P. Klein, B. Fontal, Inorg. Chem. 25 (1986) 1097.
- [6] (a) J.E. Amstrong, W.R. Robinson, R.A. Walton, J. Chem. Soc., Chem. Commun. (1981) 1120;

(b) J.E. Amstrong, W.R. Robinson, R.A. Walton, Inorg. Chem. 22 (1983) 1301;

(c) D.C. Moore, A.S. Alves, G. Wilkinson, J. Chem. Soc., Chem. Commun. (1981) 1164;

- (d) D.A. Tocher, M.D. Walkinshaw, J. Organomet. Chem. 232 (1982) C51;
- (e) T. Behing, G. Wilkinson, T.A. Stephenson, D.A. Tocher, M.D. Walkinshaw, J. Chem. Soc., Dalton Trans. (1983) 2109;
- (f) A.R. Chakravarty, F.A. Cotton, D.A. Tocher, J. Chem. Soc., Chem. Commun. (1984) 501;
- (g) F.A. Cotton, A.R. Chakravarty, D.A. Tocher, T.A. Stephenson, Inorg. Chim. Acta 87 (1984) 115;
- (h) S.M. Tetrick, V.T. Coombe, G.A. Heath, T.A. Stephenson, R.A. Walton, Inorg. Chem. 23 (1984) 4567;
- (i) A.R. Chakravarty, F.A. Cotton, D.A. Tocher, Inorg. Chem. 23 (1984) 4697;
- (j) A. Dobson, S.D. Robinson, M.F. Uttley, J. Chem. Soc., Dalton Trans. (1975) 370;
- (k) D. Robinson, M.F. Uttley, J. Chem. Soc., Dalton Trans. (1973) 1912.
- [7] R.A. Sánchez-Delgado, N. Valencia, R.-L. Márquez-Silva, A. Andriollo, M. Medina, Inorg. Chem. 25 (1986) 1106.
- [8] L. Vaska, J. Am. Chem. Soc. 88 (1966) 4100.
- [9] (a) C. De La Cruz, Norman Sheppard, J. Mol. Struct. 22 (1990) 141;
  (b) C. De La Cruz, Act. Cient. Venezolana 43 (1992) 269;
  (c) C. L. M. J. M. J. M. J. C. L. M. J. M.
  - (c) S.L. Morrison, J.J. Turner, J. Mol. Struct. 317 (1994) 39.
- [10] K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, 4th ed., Wiley–Interscience, New York, 1986.
- [11] (a) H. Topsoe, B.S. Clausen, F.E. Massoth, Hydrotreating Catalysis, Springer, Berlin, 1996;

(b) R.A. Sánchez-Delgado, in: B.R. James, P.W.N.M. van Leeuwen (Eds.), Organometallic Modeling of the Hydrodesulfurization and Hydrodenitrogenation Reactions, Kluwer Academic Publishers, Dordrecht, 2000.

- [12] (a) R.H. Fish, J.L. Tan, A.D. Thormodsen, J. Org. Chem. 49 (1984) 4500;
- (b) R.A. Sánchez-Delgado, E. González, Polyhedron 8 (1989) 1431.
- [13] (a) M. Rosales, Y. Alvarado, M. Boves, R. Rubio, R. Sánchez-Delgado, H. Soscún, Transition Met. Chem. 20 (1995) 246;
  - (b) M. Rosales, J. Navarro, L. Sánchez, A. González, Y. Alvarado, R. Rubio, C. De La Cruz, T. Rajmankina, Transition Met. Chem. 21 (1996) 11;

(c) M. Rosales, A. González, J. Navarro, H. Soscún, J. Zárraga, Inorg. Chim. Acta 257 (1997) 131;

- (d) M. Rosales, F. Arrieta, J. Castillo, A. González, J. Navarro, R. Vallejo, Stud. Surf. Sci. Catal. 130D (2000) 3357;
- (e) M. Rosales, J. Castillo, A. González, L. González, K. Molina, J. Navarro, I. Pacheco, Transition Met. Chem. 29 (2004) 221.
- [14] Y. Alvarado, M. Busolo, F. López-Linares, J. Mol. Catal. 142 (1999) 163.
- [15] A.F. Borowski, S. Sabo-Etienne, B. Donnadieu, B. Chaudret, Organometallics 22 (2003) 1630.
- [16] C. Bianchini, A. Meli, S. Moneti, W. Oberhauser, F. Vizza, V. Herrera, A. Fuentes, R.A. Sánchez-Delgado, J. Am. Chem. Soc. 121 (1999) 7071.
- [17] A.F. Borowski, S. Sabo-Etienne, B. Donnadieu, B. Chaudret, Organometallics 22 (2003) 4803.
- [18] (a) J.P. Collman, L.S. Hegedus, J.R. Norton, R.G. Finke, Principles and Applications of Organotransition Metal Chemistry, University Science Book, Mill Valley, 1988, pp. 564–567;
  (b) B. Cornils, W. A Herrmann (Eds.), Applied Homogeneous Catalysis with Organometallic Compounds, VCH, Weinhein, 1996, pp. 571–618;
  (c) S. Bhaduri, D. Mukesh, Homogeneous Catalysis. Mechanisms and Industrial Applications, Wiley, New York, 2000, pp. 55–89.
- [19] P. Van Leeuwen, C. Claver (Eds.), Rhodium Catalyzed Hydroformylation, Kluwer Academic Publishers, Dordrecht, 2000.
- [20] R.A. Sánchez-Delgado, J.S. Bradley, G. Wilkinson, J. Chem. Soc., Dalton Trans. (1976) 309.
- [21] R.A. Sánchez-Delgado, M. Rosales, A. Andriollo, Inorg. Chem. 30 (1991) 1170.
- [22] E. Cesarotti, A. Fusi, R. Lugo, G.M. Zanderighi, J. Mol. Catal. 4 (1978) 205.
- [23] P.J. Baricelli, E. Lujano, M. Modroño, A.C. Marrero, Y.M. García, A. Fuentes, R.A. Sánchez-Delgado, J. Organomet. Chem. 689 (2004) 3782.
- [24] (a) A.D. Becke, J. Chem. Phys. 98 (1993) 5648;
  (b) C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785;
  (c) B. Miehlich, A. Savin, H. Stoll, H. Preuss, Chem. Phys. Lett. 157 (1989) 200.
- [25] (a) J.B. Collins, P.V.R. Schleyer, J.S. Binkley, J.A. Pople, J. Chem. Phys. 64 (1967) 5142;
  - (b) K.D. Dobbs, W.J. Hehre, J. Comput. Chem. 8 (1987) 880;
  - (c) M.S. Gordon, Chem. Phys. Lett. 76 (1980) 163;
  - (d) K. Raghavachari, G.W. Trucks, J. Chem. Phys. 91 (1989) 1062.
- [26] M. Rosales, A. González, Y. Guerrero, I. Pacheco, R.A. Sánchez-Delgado, J. Mol. Catal. A 270 (2007) 141.
- [27] R.H. Fish, Ann. N. Y. Acad. Sci. 415 (1983) 292.