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Mononuclear ruthenium complexes containing two different phosphines in *trans* position: I. Synthesis and spectroscopic characterization

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Abstract

New mononuclear ruthenium complexes $Ru(CO)_2(Y)(Y')(P^nBu_3)[P(p\text{-}XC_6H_4)_3]$ (Y, Y′ = H, CH_3COO; X = CH_3O, CH_3, H, F, Cl), all containing a P^nBu_3 in *trans* position to a triarylphosphinic ligand differently substituted in the *para* position, were synthesized. These ligands were chosen in order to change the basicity of the phosphine in *trans* to the P^nBu_3, without relevant steric changes. Spectroscopic data of the new complexes were correlated with the basicity of the triarylphosphines or with the mesomer effect of the substituent in the *para* position of the aromatic ring. The presence of two different phosphines into a mononuclear ruthenium complex seems an interesting model to study the "*trans* effect" for octahedral species.

Keywords: Ruthenium; Mononuclear complexes; Octahedral complexes; *trans* Effect; Phosphinic ligands

1. Introduction

Recently, we have studied the reaction of the binuclear ruthenium carbonylcarboxylato $Ru_2(CO)_4(CH_3COO)_2(P^nBu_3)_2$ with acetic acid and we have observed, through NMR spectroscopy, the formation of a mononuclear specie containing a κ^1 acetato ligand and a κ^2 coordinated one, $Ru(CO)_2(\kappa^1\text{-}O\text{-}CH_3COO)(\kappa^2\text{-}O,O'\text{-}CH_3COO)(P^nBu_3)$. This complex has been used as intermediate for the synthesis of $Ru(CO)_2(CH_3COO)_2(P^nBu_3)(PPh_3)$, containing two different phosphinic ligands in *trans* position [1] (Fig. 1).

The presence of two different phosphines is an interesting model to study the "*trans* effect" for octahedral species. In fact the σ-donor and the π-acceptor ability of a ligand influence its stability in the metal coordination sphere, but also the mobility of the other ligands, particularly those in *trans* position.

The "*trans* effect" is a well-known phenomenon for ligand substitution in square-planar complexes of Pt(II) [2], Rh(I) [3], Pd(II) and Ni(II) [4], while it has been much less investigated for octahedral complexes [5]. In particular, the "*trans* influence" has been well established for ruthenium octahedral silyl complexes [5o,5p,5q,6]. The "*trans* effect" in octahedral complexes is analogous to that of square-planar ones. However, Bersuker [7] reports that the "*trans* effect" of octahedral complexes is lower and further it is complicated by the effect of *cis* neighbors and steric hindrance.

A "*trans* effect" may influence the reactivity and the catalytic activity of a mixed biphosphine-substituted mononuclear ruthenium complex. For example, in a process involving a dissociative mechanism, the synergic effect of *trans* phosphines would make easier the formation of a coordinatively unsaturated specie, available for the activation of reagents and substrates. In fact the

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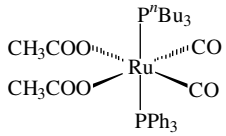


Fig. 1. Structure of $Ru(CO)_2(CH_3COO)_2(P^nBu_3)(PPh_3)$.

contemporary presence of the significantly more basic P^nBu_3 and of the good leaving ligand PPh_3 facilitates the less basic phosphine dissociation.

To study how the presence of two different phosphinic ligands on the same metal centre affects the reactivity and the catalytic activity, we have synthesized several mononuclear ruthenium complexes (Table 1), containing different *para* substituted triarylphosphinic ligands in *trans* position to the P^nBu_3 (Fig. 2).

Tolman [8] made a practical and useful separation between electronic and steric effects, introducing the cone angle ϑ and the electronic parameter χ, as measures of, respectively, the steric bulk and the electronic properties of phosphorus ligands.

The basicity of the phosphinic ligands has been often used as a measure of σ-donor power of these ligands toward transition metals [9]. In the literature, many studies are reported about the correlation between basicity of phosphines and their stereoelectronic effects. Rahman et al. [10] found a linear relation between pK_a values and χ parameters for the triarylphosphines used in our research, while it is negligible their dependence to steric effects. The pK_a values decrease with enhancement of the χ values (Table 2).

Table 1
$Ru(CO)_2(Y)(Y')(P^nBu_3)[P(p\text{-}XC_6H_4)_3]$ complexes

Code	X	Y	Y′
1a	CH_3O	CH_3COO	CH_3COO
2a		H	H
3a		H	CH_3COO
1b	CH_3	CH_3COO	CH_3COO
2b		H	H
3b		H	CH_3COO
1c	H	CH_3COO	CH_3COO
2c		H	H
3c		H	CH_3COO
1d	F	CH_3COO	CH_3COO
2d		H	H
3d		H	CH_3COO
1e	Cl	CH_3COO	CH_3COO
2e		H	H
3e		H	CH_3COO

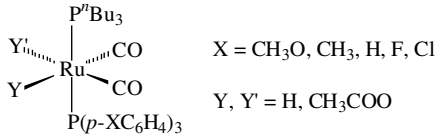


Fig. 2. Structure of $Ru(CO)_2(Y)(Y')(P^nBu_3)[P(p\text{-}XC_6H_4)_3]$.

Table 2
Steric and electronic properties of the employed phosphines[a]

Ligand	χ	pK_a	ϑ
$P(^nBu)_3$	5.25	8.43	132
$P(p\text{-}CH_3OC_6H_4)_3$	10.50	4.59	145
$P(p\text{-}CH_3C_6H_4)_3$	–	3.84	145
PPh_3	13.25	2.73	145
$P(p\text{-}FC_6H_4)_3$	15.70	1.97	145
$P(p\text{-}ClC_6H_4)_3$	16.80	1.03	145

[a] See [9d] for the discussion about phosphines basicity values.

The substituent in the *para* position of the aromatic ring gradually modulates the basicity of the triarylphosphines, without relevant steric changes. In fact, the employed triarylphosphines are characterized by the same cone angle value (ϑ), but show different pK_a values (Table 2).

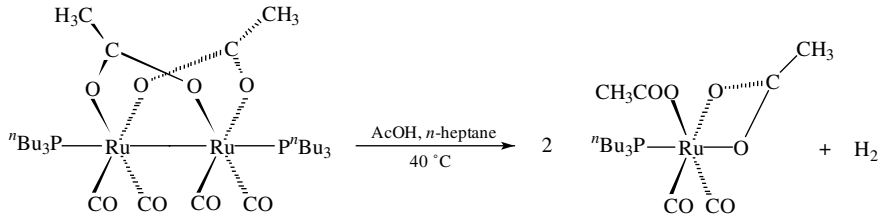
These *para* substituted triarylphosphines are useful to change the electronic contribute of the ligand, without significant steric variations.

2. Results and discussion

2.1. Synthesis of $Ru(CO)_2(CH_3COO)_2(P^nBu_3)[P(p\text{-}XC_6H_4)_3]$ (1a–1e)

$Ru(CO)_2(CH_3COO)_2(P^nBu_3)[P(p\text{-}XC_6H_4)_3]$ (**1a**–**1e**) have been synthesized from a tributylphosphine substituted binuclear ruthenium carbonylcarboxylato complex. $Ru_2(CO)_4(CH_3COO)_2(P^nBu_3)_2$ reacts at 40 °C with acetic acid [1] giving the unstable specie $Ru(CO)_2(\kappa^1\text{-}O\text{-}CH_3COO)(\kappa^2\text{-}O,O'\text{-}CH_3COO)(P^nBu_3)$, containing one κ^1 and one κ^2 acetato ligand (Scheme 1). The conversion is 100% after 48 h.

Adding an equimolecular amount of a triarylphosphine to the solution of this intermediate specie, the complexes **1a**–**1e** are obtained (Scheme 2) together with a small amount of the two mononuclear $Ru(CO)_2(CH_3COO)_2(P^nBu_3)_2$ and $Ru(CO)_2(CH_3COO)_2[P(p\text{-}XC_6H_4)_3]_2$ (**4a**–**4e**), containing two identical phosphines. The reaction is carried out at 40 °C, in order to minimize their formation. The conversion is 100% after 6 h. It is interesting to observe that a shorter time (2 h) has been sufficient for the formation of the complex **1a**, in agreement with $P(p\text{-}CH_3OC_6H_4)_3$ easier coordination to the ruthenium due to the electron donating power of the CH_3O substituent. A longer reaction time (14 days) is required to obtain the analogous complex containing the $P(OPh)_3$ in *trans* position to the P^nBu_3, due to phosphito less basicity ($pK_a = -2$).



Scheme 1.

2.2. Spectroscopic characterization of $Ru(CO)_2(CH_3COO)_2(P^nBu_3)[P(p\text{-}XC_6H_4)_3]$ (**1a–1e**)

All $Ru(CO)_2(CH_3COO)_2(P^nBu_3)[P(p\text{-}XC_6H_4)_3]$ complexes (**1a**–**1e**) have been characterized by IR and multinuclear NMR spectroscopy and the collected data are in agreement with an octahedral structure containing two phosphines in *trans* position, two *cis* carbonyl groups and two *cis* acetato ligands (Fig. 2, $Y = Y' = CH_3COO$).

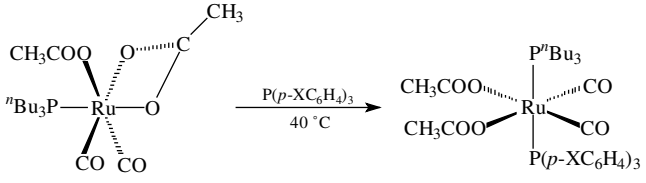
The spectroscopic data have been correlated with the basicity of the triarylphosphines or with the mesomer effect of the substituent in the *para* position of the aromatic ring.

In the IR spectra, the CO stretching frequencies for the species **1a**–**1e** are similar, nevertheless a slight reduction of the frequencies has been observed increasing the triarylphosphine basicity (Table 3).

When the σ-donor power of the phosphinic ligand increases, the electron density on the ruthenium enhances and the backdonation from the metal to the carbonyl group increases; so the bond order of the CO is reduced.

Increasing the basicity of the $P(p\text{-}XC_6H_4)_3$ the ^{31}P chemical shift of the coordinated P^nBu_3 decreases (Table 4). In fact, when the basicity of the $P(p\text{-}XC_6H_4)_3$ enhances, the strength of the Ru–P^nBu_3 bond is weaker, causing an increase of the phosphorus electron density, thus a higher shielding, and the P^nBu_3 ^{31}P δ shifts to lower frequency. It is interesting to observe that the specie $Ru(CO)_2(CH_3COO)_2(P^nBu_3)_2$ shows, in the ^{31}P NMR spectrum, a signal at 17.4 ppm, in agreement with the presence of the two more basic ligands P^nBu_3.

The ^{31}P chemical shifts (Table 4) of *para*-substituted triarylphosphines (free and coordinated) are correlated to the mesomer effect +M of the substituent in the *para* position ($CH_3O > F > Cl > CH_3 > H$). In fact, increasing the electron-donating ability of the substituent, the electron density on the *para* carbons increases and ^{31}P δ is shifted to lower values.



X = CH_3O (**1a**), CH_3 (**1b**), H (**1c**), F (**1d**), Cl (**1e**)

Scheme 2.

Table 3
IR stretching frequencies of carbonyl groups[a]

Complex	ν_{CO} (cm^{-1})	Triarylphosphine pK_a
1a	2040 (vs) 1976 (vs)	4.59
1b	2041 (vs) 1977 (vs)	3.84
1c	2042 (vs) 1979 (vs)	2.73
1d	2043 (vs) 1980 (vs)	1.97
1e	2044 (vs) 1981 (vs)	1.03
2a	2002 (s) 1961 (vs)	4.59
2b	2003 (s) 1962 (vs)	3.84
2c	2005 (s) 1964 (vs)	2.73
2d	2007 (s) 1966 (vs)	1.97
2e	2008 (s) 1967 (vs)	1.03
4a	1942	4.59
4b	1943	3.84
4c	1947	2.73
4d	1950	1.97
4e	1953	1.03

[a] Solvent: CH_2Cl_2 for **1a**–**1e** and **4a**–**4e**, C_6D_6 for **2a**–**2e**.

Table 4
^{31}P NMR δ of **1a**–**1e** and of free triarylphosphines[a]

Complex	δ P^nBu_3	δ $P(p\text{-}XC_6H_4)_3$	δ Free $P(p\text{-}XC_6H_4)_3$
1a	21.7	26.2	−10.7
1d	23.7	27.1	−9.6 (d; $J_{PF} = 4.1$ Hz)
1e	24.3	27.4	−9.0
1b	22.7	27.9	−8.3
1c	23.0	29.2	−5.8

[a] Solvent: C_6D_6.

The resonance of PPh_3 in the complex $Ru(CO)_2(CH_3COO)_2(PPh_3)_2$ (33.0 ppm) is more deshielded than in the complex **1c**, where the PPh_3 is *trans* to the more basic P^nBu_3, in agreement with the stronger "*trans* effect" of P^nBu_3.

Increasing the basicity of the triarylphosphine, the acetato CH_3 δ is less shielded (Table 5). This trend is in agreement with the ^1H NMR spectra of the complexes $Ru(CO)_2(CH_3COO)_2(P^nBu_3)_2$ and $Ru(CO)_2(CH_3COO)_2(PPh_3)_2$, having the acetato chemical shifts at 2.25 and 1.62 ppm, respectively.

Table 5
^{1}H NMR δ of **1a**–**1e** acetato groups[a]

Complex	δ	Triarylphosphine pK_a
1a	1.99	4.59
1b	1.95	3.84
1c	1.87	2.73
1d	1.85	1.97
1e	1.84	1.03

[a] Solvent: C_6D_6.

In the ^{1}H NMR spectra of all complexes, among 6.50 and 8.00 ppm, the most deshielded signal is assigned to protons in *orto* position, due to the electron-withdrawing effect of the phosphorus atom. Furthermore, when phosphorus is coordinated to the metal, there is not electron delocalization of the phosphorus lone pair on the *orto* carbons due to the mesomer effect, as in the free ligand.

The higher σ-donor ability of the phosphine reduces the electron density on the phosphorus atom which exerts a greater electron-withdrawing effect on the aromatic system. Consequently, increasing the basicity of the phosphine, the *orto* H δ shifts to higher frequencies (Table 6).

Any correlation was not found between *meta* H δ and the basicity of the coordinated phosphine P(*p*-$XC_6H_4)_3$ (Table 6).

2.3. Spectroscopic characterization of $Ru(CO)_2(CH_3COO)_2[P(p\text{-}XC_6H_4)_3]_2$ (**4a**–**4e**)

$Ru(CO)_2(CH_3COO)_2[P(p\text{-}XC_6H_4)_3]_2$ (**4a**–**4e**) complexes were found as by-products in the synthesis of $Ru(CO)_2(CH_3COO)_2(P^nBu_3)[P(p\text{-}XC_6H_4)_3]$ (**1a**–**1e**). The complexes $Ru(CO)_2(CH_3COO)_2[P(p\text{-}XC_6H_4)_3]_2$ (X = CH_3O, H) (**4a**, **4c**) were isolated and characterized through IR and multinuclear NMR spectroscopy. The elemental analysis confirmed the reported formulation.

The data collected are in agreement with an octahedral structure. The possible structures (**a**), (**c**), (**e**), reported in Fig. 3, can be ruled out according to the following considerations: the presence of a single band in the carbonyl stretching region of the IR spectra is in agreement with two carbonyl groups in *trans* position; the ^{1}H and ^{13}C NMR spectra are in agreement with two

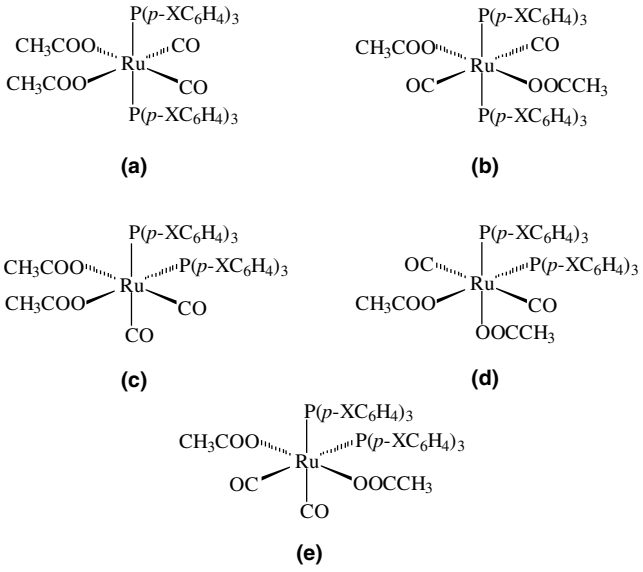


Fig. 3. Possible structures of **4a**–**4e**.

equivalent acetato ligands; the triplet at higher frequencies than 200 ppm in the ^{13}C NMR spectra may be ascribed to the carbon atoms of two equivalent carbonyl groups coupled with two *cis* phosphines; the ^{31}P NMR spectra show only one resonance, in agreement with the presence of two equivalent phosphines. With the collected spectroscopic data we are not able to discriminate among the structures (**b**) or (**d**) for these complexes.

The formation of the species $Ru(CO)_2(CH_3COO)_2[P(p\text{-}XC_6H_4)_3]_2$ (X = CH_3, F, Cl) (**4b**, **4d**, **4e**) in the synthesis of $Ru(CO)_2(CH_3COO)_2(P^nBu_3)[P(p\text{-}XC_6H_4)_3]$ (**1b**, **1d**, **1e**) has been evidenced only through IR and ^{31}P NMR spectroscopy.

Increasing the triarylphosphine basicity, the CO stretching frequency decreases (Table 3), also for the complexes **4a**–**4e**.

The ^{31}P chemical shifts of the triarylphosphines coordinated to the ruthenium (Table 7) have the same trend observed for the free phosphines (Table 4), in agreement with a mesomer effect +M of the substituent in the *para* position ($CH_3O > F > Cl > CH_3 > H$).

Table 6
^{1}H NMR δ of **1a**–**1e** phosphine aromatic rings[a]

Complex	Triarylphosphine pK_a	δ H_o	δ H_m
1a	4.59	7.96	6.77
1b	3.84	7.94	6.99
1d	1.97	7.73	6.76
1e	1.03	7.64	7.07

[a] Solvent: C_6D_6.

Table 7
^{31}P NMR δ of **4a**–**4e**[a]

Complex	δ
4a	35.5
4b	38.4
4c	39.0
4d	37.5
4e	38.3

[a] Solvent: C_6D_6.

2.4. Synthesis of $RuH_2(CO)_2(P^nBu_3)[P(p\text{-}XC_6H_4)_3]$ (2a–2e)

$Ru(CO)_2(CH_3COO)_2(P^nBu_3)[P(p\text{-}XC_6H_4)_3]$ (**1a**–**1e**) have been quantitatively transformed into the corresponding dihydride $RuH_2(CO)_2(P^nBu_3)[P(p\text{-}XC_6H_4)_3]$ (**2a**–**2e**), according to Scheme 3. These reactions have been performed into an autoclave, with 100 bar of hydrogen, at 60 °C for 14 h (**2a**, **2b**, **2d**, **2e**) or at 40 °C for 16 h (**2c**).

The formation of the dihydride complexes from the diacetato species with hydrogen is reversible, so the reaction is carried out in the presence of anhydrous sodium carbonate to neutralize the free acetic acid and to shift the equilibrium.

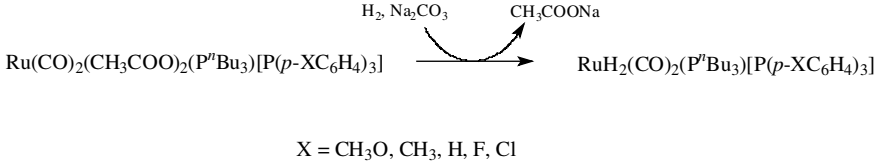
The reaction conditions have been chosen in order to have the complete conversion of **1a**–**1e**, minimizing the concomitant phosphine redistribution to give bis-tributylphosphino and bis-triarylphosphino diacetato and dihydrido complexes.

The presence of two different phosphines in the coordination sphere of the metal has a positive effect on hydrogen activation. In fact these diacetato complexes are more reactive with hydrogen than the analogous complexes containing two identical phosphines $Ru(CO)_2(CH_3COO)_2(P^nBu_3)_2$ [11] and $Ru(CO)_2(CH_3COO)_2(PPh_3)_2$ [12]: lower temperatures and shorter times are needed for **1a**–**1e** transformation into the corresponding **2a**–**2e**.

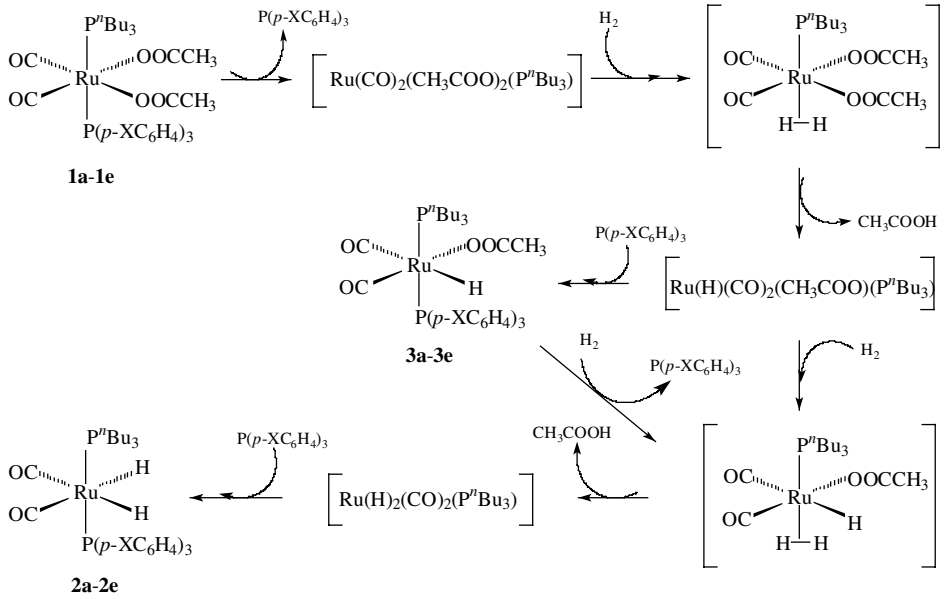
This behavior suggests the formation of dihydride complexes through the dissociation of triarylphosphine, then the formation of a dihydrogen complex, that eliminates acetic acid and finally the recoordination of the phosphinic ligand (Scheme 4). The formation of the dihydride complex is preceded by the formation of a ruthenium hydroacetate. The monohydrido complex has been evidenced in the ^{31}P and ^1H NMR spectra when the reaction with hydrogen is not completed.

$RuH(CO)_2(CH_3COO)(P^nBu_3)[P(p\text{-}CH_3OC_6H_4)_3]$ (**3a**) and $RuH(CO)_2(CH_3COO)(P^nBu_3)(PPh_3)$ (**3c**), likewise the species $RuH(CO)_2(CH_3COO)(P^nBu_3)_2$ [13] and $RuH(CO)_2(CH_3COO)(PPh_3)_2$ [14], were synthesized and characterized.

For a better characterization **3a**, **3c** (Fig. 2, Y = H, Y′ = CH_3COO), intermediates of the reaction between **1a**, **1c** and hydrogen, have been synthesized by reaction of the $RuH_2(CO)_2(P^nBu_3)[P(p\text{-}XC_6H_4)_3]$ (**2a, 2c**) with acetic acid (Scheme 5).



Scheme 3.



Scheme 4.

$$RuH_2(CO)_2(P^nBu_3)[P(p\text{-}XC_6H_4)_3] + CH_3COOH \rightleftharpoons RuH(CO)_2(CH_3COO)(P^nBu_3)[P(p\text{-}XC_6H_4)_3] + H_2$$

Scheme 5.

2.5. Spectroscopic characterization of $RuH_2(CO)_2(P^nBu_3)[P(p\text{-}XC_6H_4)_3]$ (2a–2e)

The complexes $RuH_2(CO)_2(P^nBu_3)[P(p\text{-}XC_6H_4)_3]$ (**2a**–**2e**) have been characterized through IR and multinuclear NMR spectroscopy and the collected data are in agreement with an octahedral structure containing the P^nBu_3 in *trans* position to the $P(p\text{-}XC_6H_4)_3$, two *cis* carbonyl groups and two *cis* hydridic ligands (Fig. 2, $Y = Y' = H$).

The CO stretching frequencies, in the IR spectra of the dihydride complexes, have values correlated with $P(p\text{-}XC_6H_4)_3$ pK_a (Table 3). The same explanation reported for the **1a**–**1e** CO stretching frequencies trend may be claimed.

^{31}P NMR δ trend of the two phosphinic ligands is different from that observed for the corresponding acetato complexes, showing as the distribution of electronic density in the complexes is the result of the global effect of all ligands.

In fact the presence of different $P(p\text{-}XC_6H_4)_3$ in *trans* does not seem to have any influence on δ ^{31}P values of the P^nBu_3, while chemical shifts of the $P(p\text{-}XC_6H_4)_3$ increase as the basicity of the phosphine decreases, except for PPh_3 (**2c**), that shows highest value (Table 8).

Spectroscopic data seem to indicate that the phosphines "*trans* effect" is more evident in the acetato complexes **1a**–**1e** that in the dihydride **2a**–**2e**. It is known that in octahedral complexes the "*trans* effect" can be complicated by the influence of *cis* neighbors and steric hindrance [7]. The "*trans* influence" of a ligand depends not only upon the nature and properties of the ligand itself but by the metal, its oxidation state, the other ligands and the degree of coordination of the metal.

Analogous considerations rise from the analysis of the ^1H NMR spectra. The chemical shifts of the hydrides **2a**–**2e** are among −7.73 and −6.35 ppm and, increasing the σ-donor power of the $P(p\text{-}XC_6H_4)_3$, the resonance of the hydride shifts to higher frequencies (Table 9). This trend is unexpected; in fact in ^1H NMR spectra of $RuH_2(CO)_2(P^nBu_3)_2$ and $RuH_2(CO)_2(PPh_3)_2$, the hydride δ are at −7.73 and −6.35 ppm, respectively, in agreement with the phosphine basicity.

Table 8
^{31}P NMR δ of **2a**–**2e**[a]

Complex	δ P^nBu_3	δ $P(p\text{-}XC_6H_4)_3$	Triarylphosphine pK_a
2a	35.3	49.8	4.59
2b	35.5	52.4	3.84
2c	35.6	55.6	2.73
2d	35.2	53.3	1.97
2e	35.4	54.7	1.03

[a] Solvent: C_6D_6.

Table 9
^1H NMR δ of **2a**–**2e** hydrides[a]

Complex	Triarylphosphine pK_a	δ
2a	4.59	−6.87
2b	3.8	−6.93
2c	2.73	−7.04
2d	1.97	−7.17
2e	1.03	−7.27

[a] Solvent: C_6D_6.

3. Summary

New mononuclear ruthenium complexes $Ru(CO)_2(Y)(Y')(P^nBu_3)[P(p\text{-}XC_6H_4)_3]$ (Y, $Y' = H$, CH_3COO; $X = CH_3O$, CH_3, H, F, Cl), containing two different phosphinic ligands in *trans* position, have been synthesized and spectroscopically characterized. These complexes contain, in *trans* position to the P^nBu_3, different *para* substituted triarylphosphinic ligands, having the same cone angle value, but different pK_a values. The electronic properties of these complexes change gradually, without relevant steric changes, offering an interesting model to study the "*trans* effect" in octahedral species. The presence of two different phosphines on the same metal centre affects the reactivity with hydrogen of these mixed biphosphine-substituted ruthenium complexes, that may be ascribed to "*trans* effect". In fact the complexes **1a**–**1e** react with hydrogen at lower temperatures and with shorter times with respect to the analogous $Ru(CO)_2(CH_3COO)_2(P^nBu_3)_2$ and $Ru(CO)_2(CH_3COO)_2(PPh_3)_2$.

The spectroscopic properties of these complexes $Ru(CO)_2(Y)(Y')(P^nBu_3)[P(p\text{-}XC_6H_4)_3]$ have been correlated with the triarylphosphines basicity or with the mesomer effect of the *para* substituent of the aromatic ring. The collected data indicate that the phosphines "*trans* effect" is evident above all in the acetato **1a**–**1e**. This effect may be correlated with the reactivity and the catalytic activity of these complexes.

4. Experimental

4.1. Materials

$Ru_2(CO)_4(CH_3COO)_2(P^nBu_3)_2$ was synthesised according to the procedure reported by Crooks et al. [15].

n-Hexane (95%), *n*-heptane (99%), methylene chloride (99.9%), *n*-pentane (99%), C_6D_6 (99.8%), sodium carbonate (99.5%) were reagent grade and used without further purification.

Acetic acid was distilled under nitrogen prior to use (b.p. 118 °C).

Triphenylphosphine (98%), tris(4-methoxyphenyl)-phosphine (95%), tris(4-fluorophenyl)phosphine (99%), tris(4-chlorophenyl)phosphine (97%) and tris(4-methylphenyl)phosphine (98%) were used without further purification.

4.2. Instruments

IR spectra were recorded on a FT-IR Perkin–Elmer Spectrum BX model, using the Spectrum v. 3.02.02 program. The solutions were analyzed using KBr or CaF_2 cells having 0.1 mm path.

^{1}H NMR and ^{1}H NMR COSY spectra were recorded at 399.92 MHz on a Varian Mercury 400 or at 199.985 MHz on a Varian VXR 200, using solvent residual peak as reference. ^{13}C NMR spectra were collected at 100.57 MHz on a Varian Mercury 400 and at 50.286 MHz on a Varian VXR 200, using solvent residual peak as reference. ^{31}P NMR spectra were registered at 121.421 MHz on a Varian VXR 300, using H_3PO_4 (85%) as external standard: downfield values were taken as positive. All ^{13}C and ^{31}P NMR spectra were acquired using a broad band decoupler. The solvent was choosen in order to avoid the overlap between the solvent residual peak and complex signals.

Elemental analyses were performed with a Perkin–Elmer 2400 Series II CHNS/O analyzer.

4.3. Synthetic procedure

All reactions and manipulations were performed under dry nitrogen by the Schlenk tube technique.

4.3.1. $[Ru(CO)_2(\kappa^1\text{-}O\text{-}CH_3COO)(\kappa^2\text{-}O,O'\text{-}CH_3COO)(P^nBu_3)]$

A *n*-heptane (40 mL) solution of $Ru_2(CO)_4(CH_3COO)_2(P^nBu_3)_2$ (0.4165 g; 0.498 mmol) and acetic acid (1.8 mL, 31.5 mmol) was stirred at 40 °C. The reaction mixture became colorless and the conversion was full after 48 h.

The new specie [1] was unstable in absence of acetic acid, even under nitrogen, so the *n*-heptane solution was used immediately for the subsequent synthesis of the mixed complexes.

NMR and IR data for $[Ru(CO)_2(\kappa^1\text{-}O\text{-}CH_3COO)(\kappa^2\text{-}O,O'\text{-}CH_3COO)(P^nBu_3)]$: ^{1}H NMR ($C_6D_6$, 199.985 MHz): δ 2.06 (s broad, 6H, CH_3COO), 1.63 (m, 6H, CH_2P), 1.30 (m, 6H, CH_2CH_2P), 1.16 (m, 6H, CH_3CH_2), 0.77 (m, 9H, CH_3CH_2). ^{13}C{^{1}H} NMR (C_6D_6, 50.286 MHz): δ 195.9 (m, CO), 183.0 (s, κ^2-O,O′-CH_3COO), 174.5 (s, κ^1-O-CH_3COO), 24.9 (m, CH_2CH_2P), 24.3 (s, CH_3CH_2), 24.1 (m, CH_2P), 23.5 (s, κ^1-O-CH_3COO), 20.1 (s, κ^2-O,O′-CH_3COO), 13.4 (s, CH_3CH_2). ^{31}P{^{1}H} NMR (C_6D_6, 121.421 MHz): δ 44.4 (43.5 in the presence of acetic acid). IR (*n*-heptane) 2064 (s), 1999 (vs), 1579 (w), 1517 (vw) cm^{-1} (spectrum recorded in the presence of acetic acid).

4.3.2. $Ru(CO)_2(CH_3COO)_2(P^nBu_3)[P(p\text{-}CH_3OC_6H_4)_3]$ (**1a**)

350.96 mg of tris(4-methoxyphenyl)phosphine (0.996 mmol) were added to the solution of $[Ru(CO)_2(\kappa^1\text{-}O\text{-}CH_3COO)(\kappa^2\text{-}O,O'\text{-}CH_3COO)(P^nBu_3)]$ (0.996 mmol), in acetic acid (1.8 mL) and *n*-heptane (40 mL).

The solution was stirred and heated at 40 °C, for 2 h. A pale yellow solid in small amount was formed. This solid was filtered, washed with *n*-heptane, dried and characterized as $Ru(CO)_2(CH_3COO)_2[P(p\text{-}CH_3OC_6H_4)_3]_2$ (**4a**).

The washing *n*-heptane was combined with the colorless solution; the solvent was distilled under reduced pressure (temperature lower than 40 °C). The oily residue was dissolved in CH_2Cl_2, then *n*-heptane was added. The solution was concentrated by bubbling nitrogen and the complex crystallized by cooling to −20 °C. The white solid was filtered, washed with *n*-pentane and dried under vacuum (639 mg; 0.77 mmol; yield 77.3%). The mother liquor contained $Ru(CO)_2(CH_3COO)_2(P^nBu_3)_2$.

Anal. Calc. for $C_{39}H_{54}O_9P_2Ru$ (MW = 829.863 g mol^{-1}): C, 56.45; H, 6.56. Found: C, 56.51; H, 6.50%.

NMR and IR data for **1a**: ^{1}H NMR (C_6D_6, 399.92 MHz): δ 7.96 (m, 6H, H_o, $P(p\text{-}CH_3OC_6H_4)_3$), 6.77 (m, 6H, H_m, $P(p\text{-}CH_3OC_6H_4)_3$), 3.17 (s, 9H, CH_3O), 1.99 (s, 6H, CH_3COO), 1.97 (m, 6H, CH_2P), 1.52 (m, 6H, CH_2CH_2P), 1.28 (pq, $J_{HH} = 7.3$ Hz, 6H, CH_3CH_2), 0.85 (t, $J_{HH} = 7.3$ Hz, 9H, CH_3CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.57 MHz): δ 197.8 (pt, $J_{CP} = 11.4$ Hz, CO), 176.6 (s, CH_3COO), 161.1 (d, $J_{CP} = 2.1$ Hz, C_p, $P(p\text{-}CH_3OC_6H_4)_3$), 135.7 (dd, $J_{CP} = 11.5$ Hz, $J_{CP} = 0.9$ Hz, C_o, $P(p\text{-}CH_3OC_6H_4)_3$), 122.1 (dd, $J_{CP} = 44.5$ Hz, $J_{CP} = 5.1$ Hz, C_i, $P(p\text{-}CH_3OC_6H_4)_3$), 113.8 (d, $J_{CP} = 10.4$ Hz, C_m, $P(p\text{-}CH_3OC_6H_4)_3$), 55.2 (s, CH_3O), 25.0 (d, $J_{CP} = 3.5$ Hz, CH_2CH_2P), 24.4 (d, $J_{CP} = 12.3$ Hz, CH_3CH_2), 23.6 (dd, $J_{CP} = 23.5$ Hz, $J_{CP} = 3.3$ Hz, CH_2P), 13.7 (s, CH_3CH_2), 23.1 (s, CH_3COO). ^{31}P{^{1}H} NMR (C_6D_6, 121.421 MHz): δ 26.8 (A part of an AB spin system, $J_{PP} = 322.3$ Hz, 1P, $P(p\text{-}CH_3OC_6H_4)_3$), 21.6 (B part of an AB spin system, $J_{PP} = 322.3$ Hz, 1P, P^nBu_3). IR (CH_2Cl_2) 2040 (vs), 1976 (vs), 1595 (s), 1570 (w) cm^{-1}.

4.3.3. $Ru(CO)_2(CH_3COO)_2(P^nBu_3)[P(p\text{-}CH_3C_6H_4)_3]$ (**1b**)

303.2 mg of tris(4-methylphenyl)phosphine (0.996 mmol) were added to a solution of $[Ru(CO)_2(\kappa^1\text{-}O\text{-}$

$CH_3COO)(\kappa^2$-O,O′-$CH_3COO)(P^nBu_3)]$ (0.996 mmol) in acetic acid (1.8 mL) and *n*-heptane (40 mL). The solution was stirred and heated at 40 °C, for 6 h.

The solvent and the acetic acid were distilled under reduced pressure (temperature lower than 40 °C). The yellow oily residue was dissolved in CH_2Cl_2 and *n*-heptane was added. This solution was concentrated by bubbling nitrogen and the complex was crystallized by cooling to −20 °C. A white solid product was filtered, washed with *n*-pentane and dried under vacuum, obtaining 778.7 mg of **1b**, impure for $Ru(CO)_2(CH_3COO)_2[P(p\text{-}CH_3C_6H_4)_3]_2$ (**4b**).

The solid was purified by several extractions with *n*-hexane, under nitrogen, at 40 °C. After each extraction the yellow solution was separated by filtration, under inert atmosphere. The *n*-hexane solutions were collected, cooled to −20 °C, and the white crystals (**1b**) were filtered, washed with *n*-pentane and dried under vacuum (389.4 mg; 0.50 mmol; yield 50.2%).

Further, 194.3 mg of complex **1b** was recovered by cooling to −20 °C the concentrated mother liquor, with a total yield of 74.9%.

Anal. Calc. for $C_{39}H_{54}O_6P_2Ru$ (MW = 781.87 g mol^{-1}): C, 59.91; H, 6.96. Found: C, 60.30; H, 6.97%.

NMR and IR data for **1b**: ^1H NMR (C_6D_6, 399.92 MHz): δ 7.94 (m, 6H, H_o, $P(p\text{-}CH_3C_6H_4)_3$), 6.99 (m, 6H, H_m, $P(p\text{-}CH_3C_6H_4)_3$), 1.95 (m, 21H, $P(p\text{-}CH_3C_6H_4)_3$, CH_2P, CH_3COO), 1.53 (m, 6H, CH_2CH_2P), 1.28 (m, 6H, CH_3CH_2), 0.86 (m, 9H, CH_3CH_2). ^1H NMR ($CDCl_3$, 399.92 MHz): δ 7.94 (m, 6H, H_o, $P(p\text{-}CH_3C_6H_4)_3$), 6.99 (m, 6H, H_m, $P(p\text{-}CH_3C_6H_4)_3$), 2.40 (s, 9H, $P(p\text{-}CH_3C_6H_4)_3$), 1.92 (m, 6H, CH_2P), 1.56 (s, CH_3COO), 1.51 (m, 6H, CH_2CH_2P), 1.42 (m, 6H, CH_3CH_2), 0.95 (t, $J_{HH} = 7.2$ Hz, 9H, CH_3CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.57 MHz): 197.7 (pt, $J_{CP} = 11.3$ Hz, CO), δ 176.5 (s, CH_3COO), 140.3 (d, $J_{CP} = 1.6$ Hz, C_p, $P(p\text{-}CH_3C_6H_4)_3$), 134.1 (d, $J_{CP} = 10.3$ Hz, C_o, $P(p\text{-}CH_3C_6H_4)_3$), 128.9 (d, $J_{CP} = 9.9$ Hz, C_m, $P(p\text{-}CH_3C_6H_4)_3$), 127.3 (dd, $J_{CP} = 42.1$ Hz, $J_{CP} = 4.0$ Hz, C_i, $P(p\text{-}CH_3C_6H_4)_3$), 25.0 (d, $J_{CP} = 3.5$ Hz, CH_2CH_2P), 24.4 (d, $J_{CP} = 12.4$ Hz, CH_3CH_2), 23.6 (dd, $J_{CP} = 24.0$ Hz, $J_{CP} = 2.8$ Hz, CH_2P), 23.0 (s, CH_3COO), 21.4 (s, $P(p\text{-}CH_3C_6H_4)_3$), 13.7 (s, CH_3CH_2). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.421 MHz): δ 28.1 (A part of an AB spin system, $J_{PP} = 319.8$ Hz, 1P, $P(p\text{-}CH_3C_6H_4)_3$), 22.3 (B part of an AB spin system, $J_{PP} = 319.8$ Hz, 1P, P^nBu_3). IR (CH_2Cl_2) 2041 (vs), 1977 (vs), 1598 (m) cm^{-1}.

4.3.4. $Ru(CO)_2(CH_3COO)_2(P^nBu_3)(PPh_3)$ (1c)

261 mg of triphenylphosphine (0.996 mmol) were added to a solution of $[Ru(CO)_2(\kappa^1\text{-O-}CH_3COO)(\kappa^2\text{-O,O′-}CH_3COO)(P^nBu_3)]$ (0.996 mmol), in acetic acid (1.8 mL) and *n*-heptane (40 mL).

The solution was stirred and heated at 40 °C, for 6 h. A small amount of a white solid was formed and it was filtered, washed with *n*-heptane, dried and identified as $Ru(CO)_2(CH_3COO)_2(PPh_3)_2$ (**4c**).

The washing *n*-heptane was combined with the pale yellow solution; the solvent and acetic acid were distilled under reduced pressure (temperature lower than 40 °C). *n*-Heptane was added to the oily residue, at room temperature, and the formation of a white solid (**1c**) was observed. This product was filtered, washed with *n*-pentane and dried under vacuum (321.7 mg; 0.435 mmol).

The mother liquor and the washing *n*-heptane solution were concentrated under vacuum and other 198 mg of **1c** were collected by filtration (total yield 70.6%).

The mother liquor and the washing *n*-heptane, analyzed through IR and multinuclear NMR spectroscopy, contain $Ru(CO)_2(CH_3COO)_2(P^nBu_3)_2$.

Anal. Calc. for $C_{36}H_{48}O_6P_2Ru$ (MW = 739.79 g mol^{-1}): C, 58.45; H, 6.54. Found: C, 58.36; H, 6.54%.

NMR and IR data for **1c**: ^1H NMR (C_6D_6, 399.92 MHz): δ 7.96 (m, 6H, H_o, PPh_3), 7.10 (m, 6H, H_m, PPh_3), 7.02 (m, 3H, H_p, PPh_3), 1.94 (m, 6H, CH_2P), 1.88 (s, 6H, CH_3COO), 1.49 (m, 6H, CH_2CH_2P), 1.24 (q, $J_{HH} = 7.3$ Hz, 6H, CH_3CH_2), 0.82 (t, $J_{HH} = 7.3$ Hz, 9H, CH_3CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.57 MHz): δ 197.6 (dd, $J_{CP} = 12.2$ Hz, $J_{CP} = 10.5$ Hz, CO), 176.6 (s, CH_3COO), 134.2 (d, $J_{CP} = 10.2$ Hz, C_o, PPh_3), 130.3 (dd, $J_{CP} = 40.7$ Hz, $J_{CP} = 3.2$ Hz, C_i, PPh_3), 130.3 (d, $J_{CP} = 2.2$ Hz, C_p, PPh_3), 128.2 (d, $J_{CP} = 9.6$ Hz, C_m, PPh_3), 25.0 (d, $J_{CP} = 3.7$ Hz, CH_2CH_2P), 24.4 (d, $J_{CP} = 12.6$ Hz, CH_3CH_2), 23.6 (dd, $J_{CP} = 24.6$ Hz, $J_{CP} = 2.7$ Hz, CH_2P), 23.0 (s, CH_3COO), 13.6 (s, CH_3CH_2). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.421 MHz): δ 29.7 (A part of an AB spin system, $J_{PP} = 317.4$ Hz, 1P, PPh_3), 23.0 (B part of an AB spin system, $J_{PP} = 317.4$ Hz, 1P, P^nBu_3). IR (*n*-heptane) 2044 (vs), 1982 (vs), 1624 (m) cm^{-1}.

4.3.5. $Ru(CO)_2(CH_3COO)_2(P^nBu_3)[P(p\text{-}FC_6H_4)_3]$ (1d)

315 mg of tris(4-fluorophenyl)phosphine (0.996 mmol) were added to a solution of $[Ru(CO)_2(\kappa^1\text{-O-}CH_3COO)(\kappa^2\text{-O,O′-}CH_3COO)(P^nBu_3)]$ (0.996 mmol) in acetic acid (1.8 mL) and *n*-heptane (40 mL). The solution was stirred and heated at 40 °C, for 6 h.

The solvent and the acetic acid were distilled under reduced pressure (temperature lower than 40 °C); the yellow oily residue was dissolved in CH_2Cl_2 and *n*-heptane was added. The solution was concentrated by bubbling nitrogen, at room temperature. The formed pale yellow solid was filtered, washed with *n*-pentane and dried under vacuum, obtaining 537.6 mg of **1d**, impure for $Ru(CO)_2(CH_3COO)_2[P(p\text{-}FC_6H_4)_3]_2$ (**4d**).

The solid was purified by several extractions with *n*-hexane, under nitrogen, at 40 °C. After each extraction the yellow solution was separated by hot filtration, under inert atmosphere, from the residual white solid $Ru(CO)_2(CH_3COO)_2[P(p\text{-}FC_6H_4)_3]_2$ (**4d**).

The *n*-hexane solutions collected were cooled to −20 °C and a white solid was crystallized (**1d**), filtered, washed with *n*-pentane and dried under vacuum (423.1 mg; 0.533 mmol; yield 53.5%).

Anal. Calc. for $C_{36}H_{45}O_6P_2F_3Ru$ (MW = 793.76 g mol^{-1}): C, 54.47; H, 5.71. Found: C, 54.42; H, 6.03%.

NMR and IR data for **1d**: ^1H NMR (C_6D_6, 399.92 MHz): δ 7.73 (m, 6H, H_o, P(p-FC_6H_4)$_3$), 6.76 (m, 6H, H_m, P(p-FC_6H_4)$_3$), 1.89 (m, 6H, CH_2P), 1.85 (s, 6H, CH_3COO), 1.45 (m, 6H, CH_2CH_2P), 1.25 (q, J_{HH} = 7.3 Hz, 6H, CH_3CH_2), 0.84 (t, J_{HH} = 7.3 Hz, 9H, CH_3CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.57 MHz): δ 197.3 (pt, J_{CP} = 11.4 Hz, CO), 176.6 (s, CH_3COO), 164.2 (dd, J_{CF} = 252.8 Hz, J_{CP} = 2.0 Hz, C_p, P(p-FC_6H_4)$_3$), 136.3 (ddd, J_{CP} = 11.4 Hz, J_{CF} = 8.5 Hz, J_{CP} = 1.2 Hz, C_o, P(p-FC_6H_4)$_3$), 125.9 (ddd, J_{CP} = 40.5 Hz, J_{CF} = 5.3 Hz, J_{CP} = 3.6 Hz, C_i, P(p-FC_6H_4)$_3$), 115.8 (dd, J_{CF} = 21.2 Hz, J_{CP} = 10.3 Hz, C_m, P(p-FC_6H_4)$_3$), 25.0 (d, J_{CP} = 3.3 Hz, CH_2CH_2P), 24.4 (d, J_{CP} = 12.5 Hz, CH_3CH_2), 23.6 (dd, J_{CP} = 23.8 Hz, J_{CP} = 3.9 Hz, CH_2P), 23.0 (s, CH_3COO), 13.6 (s, CH_3CH_2). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.421 MHz): δ 27.4 (A part of an AB spin system, J_{PP} = 321.1 Hz, 1P, P(p-FC_6H_4)$_3$), 23.2 (B part of an AB spin system, J_{PP} = 321.1 Hz, 1P, P^{n}Bu$_3$). IR (CH_2Cl_2) 2043 (vs), 1980 (vs), 1592 (s) cm^{-1}.

4.3.6. $Ru(CO)_2(CH_3COO)_2(P^nBu_3)[P(p\text{-}ClC_6H_4)_3]$ (**1e**)

364.17 mg of tris(4-chlorophenyl)phosphine (0.996 mmol) were added to a solution of [Ru(CO)$_2$(κ^1-O-CH_3COO)(κ^2-O,O′-CH_3COO)(P^{n}Bu$_3$)] (0.996 mmol) in acetic acid (1.8 mL) and *n*-heptane (40 mL). The solution was stirred and heated at 40 °C, for 6 h.

The solvent and the acetic acid were distilled under reduced pressure (temperature lower than 40 °C). The oily residue was dissolved in CH_2Cl_2 and *n*-heptane was added. The solution was concentrated by bubbling nitrogen and cooled to −20 °C. The white precipitate was filtered, washed with cold *n*-pentane and dried under vacuum. 614.3 mg of **1e**, impure for Ru(CO)$_2$(CH_3-COO)$_2$[P(p-ClC_6H_4)$_3$]$_2$ (**4e**), were obtained. The product was purified by an other crystallization from CH_2Cl_2/*n*-heptane at −20 °C, obtaining 528 mg of **1e** (yield 62.9%).

Anal. Calc. for $C_{36}H_{45}O_6P_2Cl_3Ru$ (MW = 843.13 g mol^{-1}): C, 51.28; H, 5.38. Found: C, 51.55; H, 5.19%.

NMR and IR data for **1e**: ^1H NMR (C_6D_6, 399.92 MHz): δ 7.64 (m, 6H, H_o, P(p-ClC_6H_4)$_3$), 7.07 (m, 6H, H_m, P(p-ClC_6H_4)$_3$), 1.87 (m, 6H, CH_2P), 1.84 (s, 6H, CH_3COO), 1.43 (m, 6H, CH_2CH_2P), 1.23 (pq, J_{HH} = 7.3 Hz, 6H, CH_3CH_2), 0.83 (t, J_{HH} = 7.3 Hz, 9H, CH_3CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.57 MHz): δ 197.1 (dd, J_{CP} = 11.9 Hz, J_{CP} = 10.3 Hz, CO), 176.7 (s, CH_3COO), 137.4 (d, J_{CP} = 2.5 Hz, C_p, P(p-ClC_6H_4)$_3$), 135.3 (dd, J_{CP} = 10.6 Hz, J_{CP} = 1.7 Hz, C_o, P(p-ClC_6H_4)$_3$), 128.9 (d, J_{CP} = 9.7 Hz, C_m, P(p-ClC_6H_4)$_3$), 128.3 (dd, J_{CP} = 39.2 Hz, J_{CP} = 5.4 Hz, C_i, P(p-ClC_6H_4)$_3$), 25.0 (d, J_{CP} = 3.4 Hz, CH_2CH_2P), 24.4 (d, J_{CP} = 13.1 Hz, CH_3CH_2), 23.6 (dd, J_{CP} = 23.9 Hz, J_{CP} = 4.0 Hz, CH_2P), 23.1 (s, CH_3COO), 13.6 (s, CH_3CH_2). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.421 MHz): δ 27.8 (A part of an AB spin system, J_{PP} = 318.6 Hz, 1P, [P(p-ClC_6H_4)$_3$]), 23.7 (B part of an AB spin system, J_{PP} = 318.6 Hz, 1P, P^{n}Bu$_3$). IR (CH_2Cl_2) 2044 (vs), 1981 (vs), 1597 (m) cm^{-1}.

4.3.7. $Ru(CO)_2(CH_3COO)_2[P(p\text{-}XC_6H_4)_3]_2$ [X = CH_3O, CH_3, H, F, Cl] (**4a–4e**)

All complexes **4a**–**4e** have been obtained as by-products in the synthesis of the corresponding **1a**–**1e** complexes.

Compounds **4a** (59 mg) and **4c** (56 mg) are insoluble in acetic acid and *n*-heptane and are separated from the reaction mixture by filtration under nitrogen. They are purified by washing with *n*-heptane.

Anal. Calc. for $C_{48}H_{48}O_{12}P_2Ru$ (**4a**) (MW = 979.92 g mol^{-1}): C, 58.83; H, 4.94. Found: C, 59.17; H, 5.28%.

NMR and IR data for **4a**: ^1H NMR (C_6D_6, 399.92 MHz): δ 7.89 (m, 12H, H_o, P(p-$CH_3OC_6H_4$)$_3$), 6.78 (m, 12H, H_m, P(p-$CH_3OC_6H_4$)$_3$), 3.18 (s, 18H, CH_3O), 1.23 (s, 6H, CH_3COO). $^{13}C\{^1H\}$ NMR (C_6D_6, 100.57 MHz): δ 209.2 (t, J_{CP} = 13.2 Hz, CO), 182.2 (s, CH_3COO), 162.5 (s, C_p, P(p-$CH_3OC_6H_4$)$_3$), 137.8 (m, C_o, P(p-$CH_3OC_6H_4$)$_3$), 123.7 (t, J_{CP} = 24.2 Hz, C_i, P(p-$CH_3OC_6H_4$)$_3$), 115.0 (m, C_m, P(p-$CH_3OC_6H_4$)$_3$), 55.6 (s, CH_3O), 23.6 (s, CH_3COO). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.421 MHz): δ 35.5. IR (CH_2Cl_2) 1942 (s), 1594 (vs), 1569 (m) cm^{-1}.

Anal. Calc. for $C_{42}H_{36}O_6P_2Ru$ (**4c**) (MW = 799.76 g mol^{-1}): C, 63.08; H, 4.54. Found: C, 62.78; H, 4.52%.

NMR and IR data for **4c**: ^1H NMR (CD_2Cl_2, 399.92 MHz): δ 7.50 (m, 30H, PPh_3), 1.50 (s, 6H, CH_3COO). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100.57 MHz): δ 207.6 (t, J_{CP} = 13.9 Hz, CO), 181.6 (s, CH_3COO), 135.0 (m, C_o, PPh_3), 130.5 (m, C_i, C_p, PPh_3), 128.4 (m, C_m, PPh_3), 22.2 (s, CH_3COO). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.421 MHz): δ 40.9. IR (CH_2Cl_2) 1947 (s), 1620 (w), 1603 (w) cm^{-1}.

Compounds **4b** (62 mg) and **4d** (105 mg) have been obtained in the synthesis of the corresponding **1b** and **1d** removing the mixed complexes by several extractions with *n*-hexane, under nitrogen, at 40 °C. The solid residue was separated by filtration, washed with *n*-pentane.

NMR and IR data for **4b**: $^{31}P\{^1H\}$ NMR (C_6D_6, 121.421 MHz): δ 38.4. IR (CH_2Cl_2) 1944 (s) cm^{-1}.

NMR and IR data for **4d**: $^{31}P\{^1H\}$ NMR (C_6D_6, 121.421 MHz): δ 37.5. IR (CH_2Cl_2) 1950 (s), 1591 (vs), 1497 (vs) cm^{-1}.

Compound **4e** (100.2 mg) was collected from the mother liquor after recrystallization of **1e** from CH_2Cl_2/*n*-heptane at −20 °C.

NMR and IR data for **4e**: $^{31}P\{^1H\}$ NMR (C_6D_6, 121.421 MHz): δ 38.3. IR (CH_2Cl_2) 1953 (s) cm^{-1}.

4.3.8. $RuH_2(CO)_2(P^nBu_3)[P(p\text{-}XC_6H_4)_3]$ [X = CH_3O, CH_3, H, F, Cl] (**2a–2e**)

These compounds were synthesized using a modification to the procedure reported by Salvini et al. [16] for $RuH_2(CO)_2(P^nBu_3)_2$.

In a glass vial 1.50×10^{-5} mol of $Ru(CO)_2(CH_3COO)_2(P^nBu_3)[P(p\text{-}XC_6H_4)_3]$ (**1a–1e**) and 150 mg of sodium carbonate were introduced. The vial was inserted in a stainless steel autoclave under nitrogen atmosphere. 2 mL of C_6D_6 were added.

Hydrogen (100 bar) was introduced in the vessel and the reactor was heated at 60 °C for 14 h (**2a**, **2b**, **2d**, **2e**), or at 40 °C for 16 h (**2c**). Then it was cooled rapidly to room temperature, the gas vented and the reaction product filtered, under nitrogen atmosphere, to eliminate residual Na_2CO_3 and CH_3COONa; the light yellow solution was transferred in a NMR tube.

IR, ^1H, ^{31}P, ^{13}C NMR spectra were then recorded. The data obtained indicated quantitative transformation of the starting complexes **1a–1e** in the corresponding dihydrides **2a–2e**. Spectroscopic analyses show the contemporary formation of small amounts of $Ru(CO)_2(CH_3COO)_2(P^nBu_3)_2$ and $RuH_2(CO)_2[P(p\text{-}XC_6H_4)_3]_2$.

NMR and IR data for **2a**: ^1H NMR (C_6D_6, 199.985 MHz): δ 7.85 (m, 6H, H_o, $P(p\text{-}CH_3OC_6H_4)_3$), 6.72 (m, 6H, H_m, $P(p\text{-}CH_3OC_6H_4)_3$), 3.18 (s, 9H, CH_3O), 1.68 (m, 6H, CH_2P), 1.36 (m, 12H, $CH_3CH_2CH_2$), 0.89 (t, $J_{HH} = 6.8$ Hz, 9H, CH_3CH_2), −6.87 (pt, 2H, *H*Ru, $J_{HP} = 23.8$ Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, 50.286 MHz): δ 203.1 (m, CO), 160.9 (s, C_p, $P(p\text{-}CH_3OC_6H_4)_3$), 135.6 (d, $J_{CP} = 13.7$ Hz, C_o, $P(p\text{-}CH_3OC_6H_4)_3$), 130.8 (m, C_i, $P(p\text{-}CH_3OC_6H_4)_3$), 113.7 (d, $J_{CP} = 10.3$ Hz, C_m, $P(p\text{-}CH_3OC_6H_4)_3$), 54.6 (s, $P(p\text{-}CH_3OC_6H_4)_3$), 32.3 (d, $J_{CP} = 27.3$ Hz, CH_2P), 26.5 (s, CH_2CH_2P), 24.6 (d, $J_{CP} = 13.7$ Hz, CH_3CH_2), 14.0 (s, CH_3CH_2). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.421 MHz): δ 49.8 (A part of an AB spin system, $J_{PP} = 215.0$ Hz, 1P, $P(p\text{-}CH_3OC_6H_4)_3$), 35.2 (B part of an AB spin system, $J_{PP} = 215.0$ Hz, 1P, P^nBu_3). IR (C_6D_6) 2036 (d), 2002 (w), 1961 (vs) cm^{-1}.

NMR and IR data for **2b**: ^1H NMR (C_6D_6, 199.985 MHz): δ 7.87 (m, 6H, H_o, $P(p\text{-}CH_3C_6H_4)_3$), 6.94 (m, 6H, H_m, $P(p\text{-}CH_3C_6H_4)_3$), 1.97 (s, 9H, $P(p\text{-}CH_3C_6H_4)_3$), 1.66 (m, 6H, CH_2P), 1.36 (m, 12H, $CH_3CH_2CH_2$), 0.89 (t, $J_{HH} = 7.2$ Hz, 9H, CH_3CH_2), −6.93 (pt, $J_{HP} = 23.8$ Hz, 2H, *H*Ru). $^{13}C\{^1H\}$ NMR (C_6D_6, 50.286 MHz): δ 202.5 (m, CO) [the C_i signal is probably overlapped with the C_p one], 138.8 (s, C_p, $P(p\text{-}CH_3C_6H_4)_3$), 133.6 (d, $J_{CP} = 10.3$ Hz, C_o, $P(p\text{-}CH_3C_6H_4)_3$), 128.4 (d, $J_{CP} = 10.3$ Hz, C_m, $P(p\text{-}CH_3C_6H_4)_3$), 31.8 (d, $J_{CP} = 27.3$ Hz, CH_2P), 26.0 (m, CH_2CH_2P), 24.2 (d, $J_{CP} = 13.7$ Hz, CH_3CH_2), 20.6 (s, $P(p\text{-}CH_3C_6H_4)_3$), 13.5 (s, CH_3CH_2). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.421 MHz): δ 52.6 (A part of an AB spin system, $J_{PP} = 213.8$ Hz, 1P, $P(p\text{-}CH_3C_6H_4)_3$), 35.5 (B part of an AB spin system, $J_{PP} = 213.8$ Hz, P^nBu_3, 1P). IR (C_6D_6) 2036 (d), 2003 (w), 1962 (vs) cm^{-1}.

NMR and IR data for **2c**: ^1H NMR (C_6D_6, 199.985 MHz): δ 7.85 (m, 6H, H_o, PPh_3), 7.10 (m, 9H, H_p, H_m, PPh_3), 1.64 (m, 12H, CH_2CH_2P), 1.31 (q, $J_{HH} = 7.8$ Hz, 6H, CH_3CH_2), 0.87 (t, $J_{HH} = 7.8$ Hz, 9H, CH_3CH_2), −7.04 (t, $J_{HP} = 23.9$ Hz, 2H, *H*Ru). $^{13}C\{^1H\}$ NMR (C_6D_6, 50.286 MHz): δ 203.6 (pt, $J_{CP} = 8.0$ Hz, CO) [the C_p signal is overlapped with the solvent peak], 135.5 (m, C_i, PPh_3), 135.0 (m, C_o, PPh_3), 130.4 (m, C_m, PPh_3), 33.2 (d, CH_2P, $J_{CP} = 27.8$ Hz), 27.4 (s, CH_2CH_2P), 25.4 (d, CH_3CH_2, $J_{CP} = 12.8$ Hz), 14.8 (s, CH_3CH_2). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.421 MHz): δ 55.6 (A part of an AB spin system, $J_{PP} = 213.6$ Hz, 1P, PPh_3), 35.6 (B part of an AB spin system, $J_{PP} = 213.6$ Hz, 1P, P^nBu_3). IR (C_6D_6) 2036 (d), 2005 (w), 1964 (vs) cm^{-1}.

NMR and IR data for **2d**: ^1H NMR (C_6D_6, 199.985 MHz): δ 7.54 (m, 6H, H_o, $P(p\text{-}FC_6H_4)_3$), 6.72 (m, 6H, H_m, $P(p\text{-}FC_6H_4)_3$), 1.62 (m, 6H, CH_2P), 1.33 (m, 12H, $CH_3CH_2CH_2$), 0.88 (t, $J_{HH} = 6.8$ Hz, 9H, CH_3CH_2), −7.17 (pt, $J_{HP} = 23.8$ Hz, 2H, *H*Ru). $^{13}C\{^1H\}$ NMR (C_6D_6, 50.286 MHz): δ 202.1 (m, CO), 163.7 (d, $J_{CF} = 256.3$ Hz, C_p, $P(p\text{-}FC_6H_4)_3$), 136.0 (m, C_o, $P(p\text{-}FC_6H_4)_3$), 134.8 (d, $J_{CP} = 10.3$ Hz, C_i, $P(p\text{-}FC_6H_4)_3$), 115.7 (m, C_m, $P(p\text{-}FC_6H_4)_3$), 32.1 (d, $J_{CP} = 27.3$, CH_2P), 26.5 (s, CH_2CH_2P), 24.7 (d, $J_{CP} = 13.6$ Hz, CH_3CH_2), 14.0 (s, CH_3CH_2). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.421 MHz): δ 53.3 (A part of an AB spin system, $J_{PP} = 212.4$ Hz, 1P, $P(p\text{-}FC_6H_4)_3$), 35.2 (B part of an AB spin system, $J_{PP} = 212.4$ Hz, 1P, P^nBu_3). IR (C_6D_6) 2036 (d), 2007 (w), 1966 (vs) cm^{-1}.

NMR and IR data for **2e**: ^1H NMR (C_6D_6, 199.985 MHz): δ 7.47 (m, 6H, H_o, $P(p\text{-}ClC_6H_4)_3$), 7.03 (m, 6H, H_m, $P(p\text{-}ClC_6H_4)_3$), 1.58 (m, 6H, CH_2P), 1.36 (m, 12H, $CH_3CH_2CH_2$), 0.87 (m, 9H, CH_3CH_2), −7.27 (pt, $J_{HP} = 23.8$ Hz, 2H, *H*Ru). $^{13}C\{^1H\}$ NMR (C_6D_6, 50.286 MHz): δ 202.5 (t, $J_{CP} = 9.3$ Hz, CO), 136.7 (s, C_p, $P(p\text{-}ClC_6H_4)_3$), 135.6 (d, $J_{CP} = 13.7$, C_o, $P(p\text{-}ClC_6H_4)_3$), 133.9 (d, $J_{CP} = 13.7$ Hz, C_i, $P(p\text{-}ClC_6H_4)_3$), 128.9 (d, $J_{CP} = 20.5$ Hz, C_m, $P(p\text{-}ClC_6H_4)_3$), 32.6 (d, $J_{CP} = 27.3$ Hz, CH_2P), 26.9 (m, CH_2CH_2P), 25.0 (d, $J_{CP} = 13.7$ Hz, CH_3CH_2), 14.4 (s, CH_3CH_2). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.421 MHz): δ 54.6 (A part of an AB spin system, $J_{PP} = 214.7$ Hz, 1P, $P(p\text{-}ClC_6H_4)_3$), 35.3 (B part of an AB spin system, $J_{PP} = 214.7$ Hz, 1P, P^nBu_3). IR (C_6D_6) 2036 (d), 2008 (w), 1967 (vs) cm^{-1}.

4.3.9. $RuH(CO)_2(CH_3COO)(P^nBu_3)[P(p\text{-}XC_6H_4)_3]$ [X = CH_3O, H] (**3a**, **3c**)

A solution of $RuH_2(CO)_2(P^nBu_3)[P(p\text{-}XC_6H_4)_3]$ (X = CH_3O, H) (**2a**, **2c**) (33 mmol) in C_6D_6 (2 mL) has been transferred in the NMR sample tube and an equimolecular amount of acetic acid was added, leaving

11 mL of free volume. The formation of the specie $RuH(CO)_2(CH_3COO)(P^nBu_3)[P(p\text{-}XC_6H_4)_3]$ (**3a**, **3c**) at room temperature was checked by ^1H and ^{31}P NMR spectroscopy. After 48 h the conversion reached 32% for **3a** and 45% for **3c** and the new complexes were spectroscopically characterized.

NMR and IR data for **3a**: ^1H NMR (C_6D_6, 399.92 MHz): δ −4.45 (pt, $J_{HP} = 20.1$ Hz, 1H, *H*Ru) (only hydride region was reported). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.421 MHz): δ 37.5 (A part of an AB spin system, $J_{PP} = 260.4$ Hz, 1P, $P(p\text{-}CH_3OC_6H_4)_3$), 29.3 (B part of an AB spin system, $J_{PP} = 260.4$ Hz, 1P, P^nBu_3).

NMR and IR data for **3c**: ^1H NMR (C_6D_6, 399.92 MHz): δ −4.20 (pt, $J_{HP} = 20.0$ Hz, 1H, *H*Ru) (only hydride region was reported). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.421 MHz): δ 43.4 (A part of an AB spin system, $J_{PP} = 254.6$ Hz, 1P, PPh_3), 30.8 (B part of an AB spin system, $J_{PP} = 254.6$ Hz, 1P, P^nBu_3).

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References

[1] A. Salvini, P. Frediani, C. Giannelli, L. Rosi, J. Organomet. Chem. 690 (2005) 371.
[2] (a) M. Cusumano, P. Marricchi, R. Romeo, V. Ricevuto, U. Belluco, Inorg. Chim. Acta 34 (1979) 169;
(b) A. Sangwoon, K. Dong Heu, P. Euisuh, Taehan Hwahakhoe Chi 28 (1984) 3;
(c) Y. Wang, Y. Hang, Khimiya 32 (1991) 301;
(d) O.V. Sizova, V.I. Baranovskii, M.I. Gel'fman, Khimiya 4 (1975) 97;
(e) M.H. Chisholm, H.C. Clark, L.E. Manzer, J.B. Stothers, J.E.H. Ward, J. Am. Chem. Soc. 95 (1973) 8574;
(f) W.J. Chenvinski, B.F.G. Johnson, J. Lewis, J.R. Norton, J. Chem. Soc., Dalton Trans. (1975) 1156;
(g) H. Motschi, P.S. Pregosin, Inorg. Chim. Acta 40 (1980) 141;
(h) S.J. Kerrison, P.J.J. Sadler, J. Chem. Soc., Dalton Trans. (1982) 2363;
(i) T.G. Appletun, M.A. Bennett, Inorg. Chem. 17 (1978) 738;
(l) A. Pidcock, R.E. Richards, L.M. Venanzi, J. Chem. Soc. A (1966) 1707;
(m) K.D. Tau, D.W. Meek, Inorg. Chem. 18 (1979) 3574;
(n) P.S. Pregosin, R. Favez, R. Roulet, T. Boschi, R.H. Michelin, R. Ros, Inorg. Chim. Acta 45 (1980) Ll;
(o) T.G. Appleton, M.A. Bennett, Inorg. Chem. 17 (1978) 738;
(p) F.H. Allen, A. Pidcock, J. Chem. Soc. A (1968) 2700;
(q) G.G. Mather, A. Pidcock, G.J.N. Rapsey, J. Chem. Soc., Dalton Trans. (1973) 2095;
(r) T.G. Appleton, H.C. Clark, L.E. Manzer, Coord. Chem. Rev. 10 (1973) 335;
(s) M.M. Gofman, V.I. Nefedov, Inorg. Chim. Acta 28 (1978) 1.
[3] G.G. Christoph, P. Blum, W.C. Liu, A. Elia, D.W. Meek, Inorg. Chem. 18 (1979) 894.
[4] A. Yamamoto, Organotransition Metal Chemistry, Fundamental Concepts and Applications, Wiley, New York, 1986.
[5] (a) A. Wojcicki, F. Basolo, J. Am. Chem. Soc. 83 (1961) 525;
(b) J. Chatt, R.G. Hayter, J. Chem. Soc. (1961) 896;
(c) F. Basolo, E.J. Bounsall, J. Proc. Chem. Soc. (1963) 366;
(d) J.B. Spencer, R.J. Myers, J. Am. Chem. Soc. 86 (1964) 522;
(e) P. Moore, F. Basolo, R.G. Pearson, Inorg. Chem. 5 (1966) 223;
(f) H.L. Bott, E.J. Bounsall, J. Chem. Soc. A (1966) 1275;
(g) R.A. Bauer, F. Basolo, J. Am. Chem. Soc. 90 (1968) 2437;
(h) R.A. Bauer, F. Basolo, Inorg. Chem. 8 (1969) 2231;
(i) W.A. Schenk, W. Buchner, Inorg. Chim. Acta 70 (1983) 189;
(j) W.A. Schenk, W. Buchner, Inorg. Chem. 23 (1984) 132;
(k) G.B. Bokii, I.B. Bersuker, Zh. Strukt. Khim. 4 (1963) 934;
(l) F. Galsboel, L. Moensted, O. Moensted, Acta Chem. Scand. 46 (1992) 43;
(m) L. Moensted, O. Moensted, Acta Chem. Scand. A 38 (1984) 67;
(n) R. Poli, J.C. Gordon, Inorg. Chem. 30 (1991) 4550;
(o) R.K. Pomeroy, R.S. Gay, G.O. Evans, W.A.G. Graham, J. Am. Chem. Soc. 94 (1972) 272;
(p) R.K. Pomeroy, J. Organomet. Chem. 177 (1979) C27;
(q) R.K. Pomeroy, K.S. Wijesekera, Inorg. Chem. 19 (1980) 3729;
(r) R.K. Pomeroy, X. Hu, Can. J. Chem. 60 (1982) 1279;
(s) R.N. Haszeldine, R.V. Parish, J.H. Setchfield, J. Organomet. Chem. 57 (1973) 279.
[6] (a) M.M. Crozat, S.F. Watkins, J. Chem. Soc., Dalton Trans. (1972) 2512;
(b) R.D. Holmes-Smith, S.R. Stobart, R. Vefghi, M.J. Zaworotko, K. Jochem, T.S. Cameron, J. Chem. Soc., Dalton Trans. (1987) 969;
(c) V.K. Dioumaev, L.J. Procopio, P.J. Carroll, D.H. Berry, J. Am. Chem. Soc. 125 (2003) 8043.
[7] I.B. Bersuker, Zh. Neorg. Khim. 9 (1964) 36.
[8] (a) C.A. Tolman, Chem. Rev. 77 (1977) 313;
(b) C.A. Tolman, J. Am. Chem. Soc. 92 (1970) 2953.
[9] (a) Md.M. Rahman, H.Y. Liu, A. Prock, W.P. Giering, Organometallics 6 (1987) 650;
(b) M.N. Golovin, Md.M. Rahman, J.E. Belmonte, W.P. Giering, Organometallics 4 (1985) 1981;
(c) W.A. Henderson, C.A. Streuli, J. Am. Chem. Soc. 82 (1960) 5791;
(d) T. Allman, R.G. Goel, Can. J. Chem. 60 (1982) 716;
(e) R.A. Jackson, R. Kanluen, A. Poë, Inorg. Chem. 23 (1984) 523;
(f) C.A. Streuli, Anal. Chem. 31 (1959) 1652;
(g) K. Dahlinger, F. Falcone, A. Poë, J. Inorg. Chem. 25 (1986) 2654.
[10] Md.M. Rahman, H.Y. Liu, K. Eriks, A. Prock, W.P. Giering, Organometallics (1989) 8.
[11] P. Frediani, M. Bianchi, A. Salvini, F. Piacenti, S. Ianelli, M. Nardelli, J. Chem. Soc., Dalton Trans. (1990) 165.
[12] P. Frediani, C. Faggi, A. Salvini, M. Bianchi, F. Piacenti, Inorg. Chim. Acta 272 (1998) 141.
[13] P. Frediani, A. Salvini, M. Bianchi, F. Piacenti, J. Organomet. Chem. 454 (1993) C17.
[14] P. Frediani, C. Faggi, S. Papaleo, A. Salvini, M. Bianchi, F. Piacenti, S. Ianelli, M. Nardelli, J. Organomet. Chem. 536 (1997) 123.
[15] G.R. Crooks, B.F.G. Johnson, J. Lewis, I.G. Williams, G. Gamlen, J. Chem. Soc. A (1969) 2761.
[16] A. Salvini, P. Frediani, M. Bianchi, F. Piacenti, Inorg. Chim. Acta 227 (1994) 247.