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Reactions of dicarboxylic acids with $[Ru(CO)_3(PPh_3)_2]$

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Abstract

To obtain water soluble transition-metal complexes, complexes obtained by reaction between $[Ru(CO)_3(PPh_3)_2]$ and dicarboxylic acids have been studied. The derivative obtained with oxalic acid, $[Ru(O_2CCO_2H)_2(CO)_2(PPh_3)_2]$ (2), dissolves in water when treated with NEt_3 and reacts with $[Pt(PPh_3)_3]$ to give $[Ru(CO)_2(PPh_3)_2(\mu\text{-}O_2CCO_2)_2Pt(PPh_3)_2]$ (5).

1. Summary

By reaction of $[Ru(CO)_3(PPh_3)_2]$ (1) with oxalic acid, the derivative $[Ru(O_2CCO_2H)_2(CO)_2(PPh_3)_2]$ (2) was obtained. Compound **1** reacts with maleic acid and with fumaric acid to give the complexes $[Ru(O_2CCH{=}CHCO_2)(CO)_2(PPh_3)_2]$ (3) and $[\{Ru(CO)_2(PPh_3)(\mu\text{-}O_2CCH{=}CHCO_2)\}_2]$ (4), respectively. Compound **2** dissolves in water when treated with a base and it precipitates upon acidification of the solution. After reaction of **2** with $[Pt(PPh_3)_3]$, the complex $[Ru(CO)_2(PPh_3)_2(\mu\text{-}O_2CCO_2)_2\ Pt(PPh_3)_2]$ (5) has been isolated. Compound **5** is unstable in solution, giving the known derivative $[Pt(O_2CCO_2)(PPh_3)_2]$ (6) and a mixture in which the complex $[Ru(O_2CCO_2)(CO)_2(PPh_3)_2]$ (7) is probably present. When **3** reacts with $[Pt(PPh_3)_3]$, the olefinic double bond does not coordinate to platinum. Attempts to obtain crystals of **5** suitable for an X-ray structural determination were unsuccessful.

2. Introduction

The synthesis of $[Ru(CO)_3(PPh_3)_2]$ (1) and its oxidative addition reactions with several reagents, including trifluoroacetic acid, represents one of the milestones of modern organometallic chemistry [1]. The reactions of **1** with a series of monocarboxylic acids have given monomeric complexes of the type $[Ru(O_2CR)_2(CO)_2(PPh_3)_2]$ with a structure involving a *cis*-arrangement of both carbonyl groups and phosphine ligands and a *trans*-arrangement of the two monodentate RCO_2 ligands [2].

Ruthenium complexes of the type $[Ru(O_2CR_F)_2(CO)(PPh_3)_2]$ ($CR_F = CF_3$, C_2F_5, or C_6F_5), with one chelating and one monodentate R_FCO_2 ligand, are catalysts for the dehydrogenation of primary and secondary alcohols to aldehydes and ketones, respectively [3], and intramolecular monodentate–bidentate carboxylate ligand exchange has been observed [4]. Hydridodicarboxylic acid derivatives of ruthenium, $[\{RuH(PPh_3)_2L\}_2\{\mu\text{-}O_2C(CH_2)_nCO_2\}]$($L = PPh_3$ or CO; $n =$ 2, 3 or 4), obtained by reaction of $[RuH_2(PPh_3)_4]$ and $[RuH_2(CO)(PPh_3)_3]$ with dicarboxylic acids, are also known, and they are effective catalysts for the hydrogenation and isomerization of alkenes [5], these derivatives have chelating carboxylate ligands.

We have previously studied the reactivity of compound **1** and of its more reactive homologue $[Ru(CO)_2(PPh_3)_3]$, with several reagents [6,7]. We therefore decided to investigate the oxidative addition reactions of **1** with dicarboxylic acids, and the results are here reported. The aim of this research was to functionalise the ruthenium complexes to give compounds soluble in water and able to behave as ligands.

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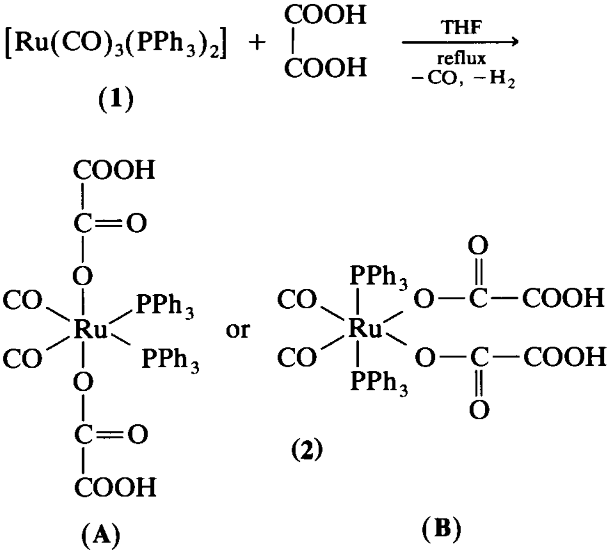
3. Results and discussion

3.1. Reactions of 1 with dicarboxylic acids

By reaction of **1** with oxalic acid in THF, the white compound **2** was obtained (eqn. (1); Table 1):

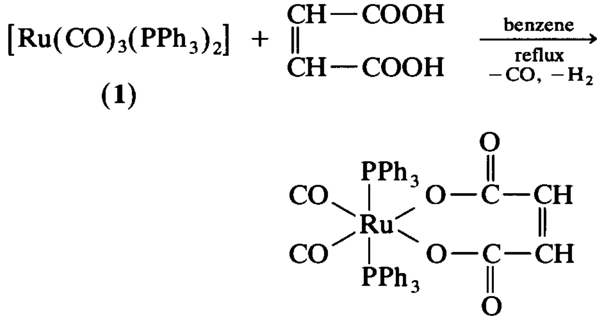


(1)

Compound **2** shows two ν(CO) stretching frequencies in the expected region for a ruthenium(II) derivative with *cis*-carbonyl ligands (Table 2), a ν(C=O) at 1775 cm^{-1}, attributable to uncoordinated carboxylic groups, while $\nu(CO_{asym})$ and $\nu(CO_{sym})$ have been observed at 1635 and 1277 cm^{-1} respectively, with a separation of *ca.* 350 cm^{-1}, which is indicative of molecules containing unidentate carboxylato groups [2]. Compound **2** shows also a band at 3296 cm^{-1} attributable to ν(OH). In the ^{1}H NMR spectrum (Table 2), a broad band at 3.4 ppm was detected; this band disappeared upon treatment with D_2O, confirming the presence of free OH groups in **2**. In the ^{31}P NMR spectrum a singlet was observed at 28.1 ppm, while the ^{13}C NMR spectrum showed the expected signals for two equivalent carbonyl groups bound to a metal (triplet, $J(C-P) = 11$ Hz), two equivalent C=O groups of the bound carboxylic functions, and two equivalent C=O groups of the uncoordinated carboxylic groups (Table 2). The presence of THF in compound **2** was confirmed by both ^{1}H and ^{13}C NMR spectra.

Structure **A** has been suggested for the homologous monocarboxylic acid derivative [2]. However the presence of a triplet in ^{13}C NMR spectrum due to the coupling of metal carbonyl combinations with two equivalent ^{31}P nuclei confirmed structure **B** for compound **2**. This structure was suggested also by the reactivity of **2** with $[Pt(PPh_3)_3]$ (see later).

After reaction of **1** with maleic acid, the white monomeric carboxylato-derivative **3** was isolated (eqn. (2); Table 1):

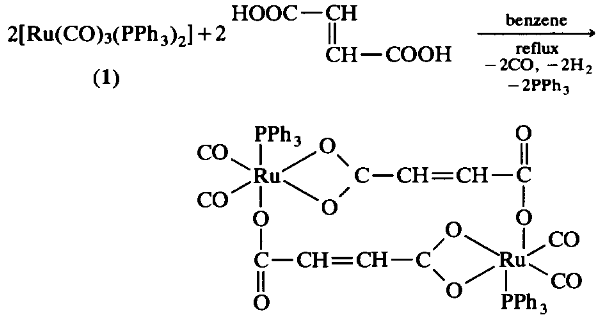


(2)

(3)

The spectroscopic data for **3** (Table 2) indicate the presence of *cis*-carbonyl ligands, monodentate carboxylate groups, equivalent hydrogen atoms of the uncoordinate olefinic function (no P–H coupling was detected, with a small shift to lower field with respect to the free donor. Coordination to a metal in a low oxidation state causes shifts of the resonances of the olefinic hydrogen atoms [8]). The rather high value of $\nu(C{=}O_{asym})$ of the coordinated carboxylate groups is reminiscent of the effect observed in acid anhydrides compared to carboxylate groups [9].

The reaction of **1** with fumaric acid gave the white dinuclear carboxylate derivative **4** (eqn. (3); Table 2):



(3)

(4)

In this case the *trans*-conformation of the organic acid imposes the bridging structure on the complex.

The dimeric structure is supported by the fact that the spectral data for **4** (Table 2) are significantly different from those of **3**. Moreover the mass spectrum has confirmed the dimeric nature of **4**. IR spectra indicate the presence of both mono- and bi-dentate carboxylate ligands. The high value of $\nu(CO_{asym})$ at 1709 cm^{-1} and its large separation from $\nu(CO_{sym})$ at 1257 cm^{-1} is indicative of monodentate coordination; on the other hand $\nu(CO_{asym})$ at 1636 and $\nu(CO_{sym})$ at 1436 cm^{-1} can be assigned to a bidentate carboxylate [10] (Table 2).

TABLE 1. Physical and analytical data

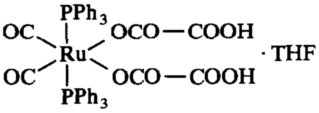
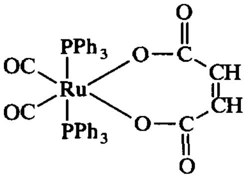
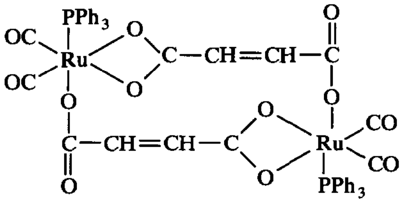
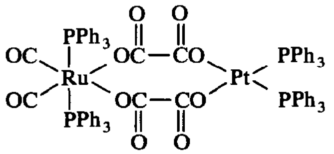
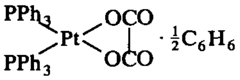
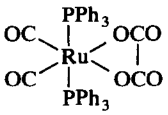
Compound		Colour	M.p. (°C)	Analyses (Found (calc.) (%))	
				C	H
	(2)	white	240	59.4 (59.3)	4.1 (4.3)
	(3)	white	190	62.9 (63.4)	4.1 (4.1)
	(4)	white	270 (dec)	55.0 (54.0)	3.3 (3.2)
	(5)	white	240	59.7 (59.4)	4.0 (3.8)
	(6)	white	-	58.5 (58.1)	3.8 (3.9)
	(7)	yellow	-	61.0 (62.4)	3.9 (3.8)

TABLE 2. Infrared (cm^{-1}, in Nujol), ^1H, ^{13}C and ^{31}P NMR data (ppm)

Compound	IR					NMR			Solvent
	ν(OH)	ν(CO)	ν(C=O)	ν(C–O)	ν(C=C)	^1H	^{13}C	^{31}P	
Oxalic acid [b]	3422	–	1695	1244	–	6.95 [a]	–	–	DMSO
2	3296	2054	1775	1277	–	3.4 (s) [a]	196 [c]	28.1 (s)	DMSO
		2001	1635				163–160		
Maleic acid [b]	3150	–	1702	1264	1636	6.25 (s), 12.4 [a]	–	–	DMSO
3	–	2060	1716	1325	1629	5.70 (s)	–	32.4 (s)	$CDCl_3$
		2001							
Fumaric acid [b]	3150	–	1676	1271	1576	6.6 (s), 12.8 [a]	–	–	DMSO
4	–	2047	1709	1257	1589	6.64 (s)	–	21 (s)	DMSO
		1994	1636	1436					
5	–	2056	1698–1676	–	–	–	162–196	8.16 (s) [d]	$CDCl_3$
		1998	1651–1644					25.7 (s)	
6	–	–	1710	1350	–	–	165	8.14 (s) [e]	$CDCl_3$
			1675						
7		2057	1698	–	–	–	163–196	25.7 (s)	$CDCl_3$
		1998							

[a] This signal disappeared on treatment with D_2O. [b] Signals due to free oxalic, maleic, and fumaric acids, respectively. [c] Triplet J(C–P) = 11 Hz. [d] J(Pt–P) = 3772 Hz. [e] J(Pt–P) = 3812 Hz.

3.2. Reactivity of compounds 2 and 3

Compound **2** is insoluble in water. However when a base such as NEt_3 is added to the suspension it dissolves. Upon acidification with hydrochloric acid the starting compound is reobtained. An acid–base reaction is obviously involved (eqn. 4):

$$[Ru(O_2CCOOH)_2(CO)_2(PPh_3)_2] \underset{HCl}{\overset{NEt_3/H_2O}{\rightleftharpoons}} [NEt_3H]_2[Ru(O_2CCOO)_2(CO)_2(PPh_3)_2] \quad (4)$$

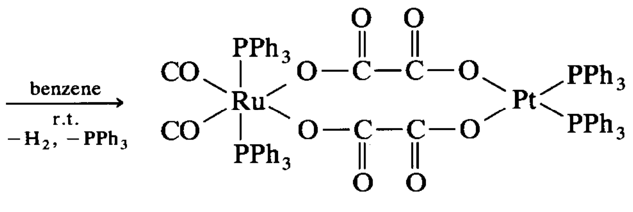
Recently there has been great interest in synthesising transition metal complexes soluble in water and showing catalytic properties [11]. The main advantage of using an aqueous/organic biphase reaction mixture lies in the easy and practically complete recovery of the metal catalyst. Catalysts whose water-solubility is based on the presence of COOH, NH_2 and SO_3H groups in the ligand appear also to be gaining importance in catalytic processes [12] and in the stabilization of metal colloids [13].

Complexes having triphenylphosphine ligands bearing sulfonic acid groups on the phenyl rings have been used as catalysts [14]; spectroscopic evidence suggests that the M–P bond of sulphonated phosphines is quite similar to those of non-sulphonated PPh_3. Nevertheless such ligands should differ significantly in their steric influence.

Our results that oxalic acid is able to induce water solubility to otherwise completely insoluble compounds, might be useful.

Compound **2** also behaves as a dicarboxylic acid when it reacts with a base such as $[Pt(PPh_3)_3]$ [15] (eqn. (5)):

$[Ru(O_2CCOOH)_2(CO)_2(PPh_3)_2] + [Pt(PPh_3)_3]$



(5)

(5)

Compound **5** (Table 1) shows the expected absorptions in the IR spectrum (Table 2). In particular there are four $\nu(C{=}O_{asym})$ bands, due to the carboxylate groups bound to two different metals. The ν(CO) values indicate a *cis*-arrangement of the carbonyls. The ^{31}P NMR spectrum has shown a singlet at 8.16 ppm, with satellite bands due to coupling to ^{195}Pt, and a singlet at 25.7 ppm due to the two phosphines bound to ruthenium.

Compound **5** is unstable in warm solution, but even at room temperature it slowly decomposes. For this reason crystals for an X-ray structural determination of **5** were not obtained. In fact, from solutions in benzene/methanol and hexane, fine crystals of two different compounds **6** and **7** were isolated (see later), and from a warm solution of **5** in benzene it was possible to isolate the white known $[Pt(O_2CCO_2)(PPh_3)_2]$ [16] (**6**) in a pure form.

In the yellow, residual mixture, compound **6** and a complex of probable composition $[Ru(O_2CCO_2)(CO)_2(PPh_3)_2]$ (**7**) (see Experimental), were detected. The oxalato ligands in **6** and **7** could be formed by C–C coupling of the two bridging oxalato ligands in **5**, but there is no evidence for this.

Finally when **3** was treated with $[Pt(PPh_3)_3]$ in benzene at reflux under a dinitrogen atmosphere, it was recovered unchanged, together with a small amount of a compound which does not contain Pt. Thus the double bond in **3** is not able to coordinate to platinum(0) in $[Pt(PPh_3)_3]$, which, on the other hand, is known readily to bind activated alkenes [8,15].

4. Experimental details

All the reactions were carried out under dinitrogen with magnetic stirring. $[Ru(CO)_3(PPh_3)_2]$ was prepared as described in the literature [17]. IR spectra were recorded on a Nicolet FT IR. NMR spectra were recorded on a Bruker AMX 400, a Bruker AC 200 and a Bruker WP 80. Elemental analyses were carried out by the Analytical Laboratories of Milan University.

4.1. Reaction between $[Ru(CO)_3(PPh_3)_2]$ (1) and oxalic acid

To $[Ru(CO)_3(PPh_3)_2]$ (**1**) (200 mg, 0.28 mmol) in anhydrous THF (20 ml), $H_2C_2O_4$ (172 mg, 1.9 mmol) was added. The yellow solution was heated under reflux for 6 h, then was left for one night under magnetic stirring. The white precipitate of **2** was filtered off, washed with THF, and dried *in vacuo* (20% yield), m.p. 240°C.

4.2. Reaction between $[Ru(CO)_3(PPh_3)_2]$ (1) and maleic acid

To a solution of $[Ru(CO)_3(PPh_3)_2]$ (**1**) (250 mg, 0.35 mmol) in benzene (15 ml), *cis*-$C_4H_4O_4$ (75 mg, 0.65 mmol) was added. The solution was heated under reflux for 4 h, then evaporated to half of its volume and hexane was added. The white precipitate of **3** was filtered off and dried *in vacuo* (70% yield), m.p. 190°C.

4.3. Reaction between $[Ru(CO)_3(PPh_3)_2]$ (1) and fumaric acid

To $[Ru(CO)_3(PPh_3)_2]$ (**1**) (250 mg, 0.35 mmol) in benzene (15 ml), *trans*-$C_4H_4O_4$ (75 mg, 0.65 mmol) was added. The yellow solution was heated under reflux for 5 h. The white precipitate of **4** was filtered off, washed with benzene and dried *in vacuo* (40% yield), m.p. 270°C (dec.)

4.4. Reaction between 2 and [Pt(PPh_3)$_3$]

To a mixture of benzene (10 ml) and ethanol (2 ml), compound **2** (158 mg, 0.18 mmol) and [Pt(PPh_3)$_3$] (177 mg, 0.18 mmol) were added. The suspension was gently heated under reflux until it became yellow (about 3 h). It was evaporated to half volume and, after cooling, a white precipitate of **5** formed. It was filtered off, crystallized from benzene/hexane, and dried *in vacuo*.

To the mother liquor hexane was added. The yellow precipitate was a mixture of a white and a yellow compound. We isolated the white compound by dissolving the mixture in benzene and, after cooling, the white compound [Pt(O_2CCO_2)(PPh_3)$_2$] (**6**) precipitated.

Attempts to isolate the yellow compound [Ru(CO)$_2$(PPh_3)$_2$(O_2CCO_2)] (**7**) in a pure form were unsuccessful, due to the presence of **6** (Table 1).

4.5. Reaction between 3 and [Pt(PPh_3)$_3$]

To compound **3** (190 mg, 0.24 mmol) in benzene (10 ml), [Pt(PPh_3)$_3$] (235 mg, 0.24 mmol) was added. The suspension was heated under reflux for 3 h and became a yellow solution. After cooling, hexane was added, and the white precipitate was filtered off, crystallized from benzene/hexane, and dried *in vacuo*.

The compound was confirmed as a mixture of **3** and a compound not containing a platinum derivative, because its ^{31}P NMR spectrum shows no ^{195}Pt satellites.

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