

The reaction of dihydridotetrakis(triphenylphosphane)ruthenium(II) with methyl acrylate. Crystal structure of bis(methylacrylate)bis(triphenylphosphane)(aqua)ruthenium(0)

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Abstract

The complex $\text{H}_2\text{Ru}(\text{PPh}_3)_4$ reacts with methyl acrylate to give bis(methylacrylate)bis(triphenylphosphane)ruthenium(0). Temperature-dependent NMR spectra show that the complex exists in two isomeric forms in solution. The major form (ca. 74%) has one methyl acrylate ligand η^2 -coordinated and the other η^4 -coordinated as a 1-oxabutadiene ligand. This complex reacts with water to give the mono-aqua adduct, the crystal structure of which is reported.

Key words: Ruthenium; Methyl acrylate; Crystal structure; X-ray diffraction

1. Introduction

Hydrido- and olefin-coordinated complexes of transition metals are generally regarded as active intermediates in catalytic transformations of olefins. For instance, dihydridotetrakis(triphenylphosphane)ruthenium(II) (**1**) is used as a precatalyst or as the active catalyst in a wide range of reactions, such as hydrogenation [1], hydroformylation [2], CC-coupling [3], and polymerization [4]. It also produces a number of complexes on reaction with various olefins [5–8]; these reactions are normally accompanied by hydrogenation of the olefin.

The reaction of $\text{H}_2\text{Ru}(\text{PPh}_3)_4$ with ethylene yields a monoolefin complex, $\text{HRu}(o\text{-C}_6\text{H}_4\text{PPh}_2)(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$, which is stabilized by *ortho*-metallation. This complex exists in two isomeric forms [8]. With propene, $\text{Ru}(\eta^3\text{-C}_3\text{H}_5)_2(\text{PPh}_3)_2$ is formed [8,9], whilst 1-butene and butadiene give $\text{Ru}(\eta^4\text{-C}_4\text{H}_6)(\text{PPh}_3)_3$, which reacts further with butadiene to give $\text{Ru}(\eta^4\text{-C}_4\text{H}_6)_2(\text{PPh}_3)$ [8]. Whereas 2-pentene and cyclohexene do not react with $\text{H}_2\text{Ru}(\text{PPh}_3)_4$, 1,5-cyclooctadiene yields the η^5 -1,5-cyclooctadienyl complex $\text{Ru}(\eta^5\text{-C}_8\text{H}_5)(o\text{-C}_6\text{H}_4\text{PPh}_2)(\text{PPh}_3)$ [8]. A characteristic feature of these 18

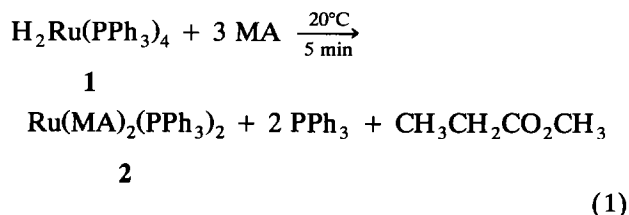
electron complexes is their yellow colour. In contrast $\text{H}_2\text{Ru}(\text{PPh}_3)_4$ forms the red 16-electron ruthenium(0) complex $\text{Ru}(\eta^2\text{-C}_8\text{H}_8)(\text{PPh}_3)_2$ with styrene [10,11]. The complex $\text{H}_2\text{Ru}(\text{PPh}_3)_4$ also reacts with electron-deficient olefins such as alkyl methacrylates. In this reaction $\text{HRu}(\text{CHC}(\text{CH}_3)\text{C}(\text{O})\text{OR})(\text{PPh}_3)_3$ is formed by C–H bond cleavage [12], and a ruthenium- π -complex is assumed to be an intermediate. In the case of methyl methacrylate this reaction is accompanied by the formation of small amounts of poly(methylmethacrylate). According to Komiya *et al.* [4], $\text{H}_2\text{Ru}(\text{PPh}_3)_4$ initiates the polymerization of olefins that are more electronegative than methyl methacrylate, such as acrylonitrile, methacrylonitrile, acrolein, methyl vinylketone and methyl acrylate. However, during our investigation [13] of ruthenium-catalyzed methyl acrylate dimerizations we were not able to confirm the polymerization of methyl acrylate by $\text{H}_2\text{Ru}(\text{PPh}_3)_4$ but we did isolate a new olefin-ruthenium(0) complex. We report below on the formation, structure and properties of this ruthenium(0) complex of methyl acrylate.

2. Results and discussion

The complex $\text{H}_2\text{Ru}(\text{PPh}_3)_4$ (**1**) reacted with neat methyl acrylate (MA) to yield a deep red solution of

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$\text{Ru}(\text{MA})_2(\text{PPh}_3)_2$ (**2**). A $^1\text{H-NMR}$ spectroscopic investigation of this reaction showed that one equiv of methyl acrylate was hydrogenated with release of two equiv of triphenylphosphane (eqn. (1)).



From the reaction mixture **2** was isolated in a yield of 82% as a yellow, fairly air-stable powder (see Experimental section). Complex **2** seemed to react very efficiently with traces of water, because red crystals of a mono-aqua adduct were isolated from a toluene/*n*-hexane solution after 90 days. This was confirmed by addition of small amounts of water to a solution of **2** in toluene/hexane, which led to a fairly rapid (< 1 day) crystallization of **2aq**.

2.1. The molecular structure of $\text{Ru}(\text{MA})_2(\text{PPh}_3)_2(\text{H}_2\text{O})$ (**2aq**)

Crystals of **2aq** were subjected to an X-ray structure analysis. The monoclinic unit cell of **2aq** contains 8 mononuclear ruthenium complex molecules, which are arranged in pairs, related by the inversion centre. An ORTEP plot of the molecular structure of one ruthenium complex is shown in Fig. 1. Selected geometrical parameters are listed in Tables 1–3.

The coordination geometry around the ruthenium atom can be described as a trigonal bipyramid in which

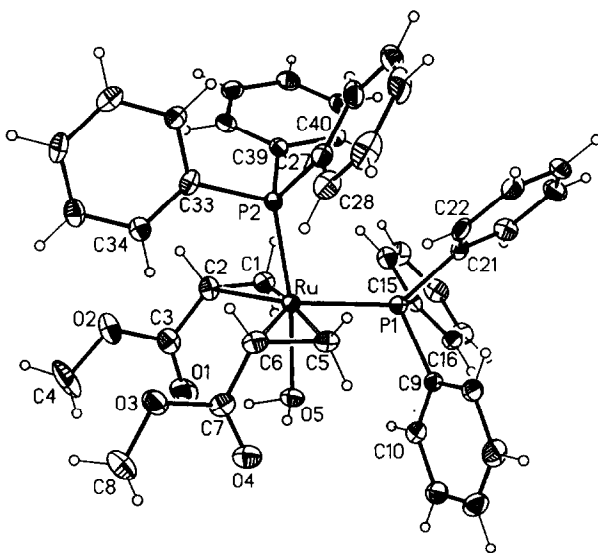


Fig. 1. Molecular structure of **2aq**.

TABLE 1. Selected bond lengths (pm) and atom distances (pm) in **2aq**

Ru–P(1)	241.4(1)	Ru–P(2)	227.1(1)
Ru–C(1)	215.0(4)	Ru–C(5)	214.1(4)
Ru–C(2)	221.3(3)	Ru–C(6)	218.9(4)
Ru–O(5)	220.1(3)		
C(1)–C(2)	141.3(6)	C(5)–C(6)	143.1(6)
C(2)–C(3)	145.6(7)	C(6)–C(7)	144.5(7)
C(3)–O(1)	123.1(5)	C(7)–O(4)	121.3(5)
C(3)–O(2)	134.0(5)	C(7)–O(3)	136.7(5)
O(2)–C(4)	144.5(8)	O(3)–C(8)	144.6(7)
P(1)–C(9)	186.6(3)	P(2)–C(27)	186.8(3)
P(1)–C(15)	185.8(2)	P(2)–C(33)	187.6(2)
P(1)–C(21)	185.2(3)	P(2)–C(39)	184.5(3)
O(5)–O(1)	259.4(5)	O(5)–O(4)	268.4(5)

ruthenium is located above the equatorial plane {C(1)–C(2)–P(1)–C(5)–C(6)} formed by one triphenylphosphane and two methyl acrylate ligands (Fig. 1). The second triphenylphosphane ligand adopts a position almost orthogonal (P(1)–Ru–P(2) = 105.5°) to this plane. The coordinated water molecule is located *trans* to the axially oriented triphenylphosphane. The Ru–O(5) bond length of 220.2 pm is comparable to the Ru–O bond lengths to the acetate ligand (220.8, 219.8 pm) in $\text{HRu}(\text{O}_2\text{CCH}_3)(\text{PPh}_3)_3$ [14].

The two Ru–P bond lengths are markedly different: the equatorial Ru–P(1) distance is 14.3 pm longer than the axial Ru–P(2) distance. As a result of the coordination to ruthenium the C(1)–C(2) (141.3 pm) and C(5)–C(6) (143.1 pm) bond lengths of the complexed methyl acrylate ligands are elongated by about 6 pm compared with those in uncoordinated methyl acrylate (136.1 pm) [15]. The verticals from the ruthenium atom to the C=C

TABLE 2. Selected bond angles (°) and non-bonding angles (°) in **2aq**

C(1)–Ru–P(1)	89.9(1)	C(5)–Ru–P(1)	85.6(1)
C(2)–Ru–P(1)	127.6(1)	C(6)–Ru–P(1)	123.8(1)
C(1)–Ru–P(2)	93.5(1)	C(5)–Ru–P(2)	96.4(1)
C(2)–Ru–P(2)	85.5(1)	C(6)–Ru–P(2)	90.1(1)
C(1)–Ru–O(5)	81.9(1)	C(5)–Ru–O(5)	88.5(1)
C(2)–Ru–O(5)	86.3(1)	C(6)–Ru–O(5)	89.4(1)
C(1)–Ru–C(6)	143.7(2)	C(2)–Ru–C(5)	145.2(1)
C(1)–Ru–C(5)	169.9(1)	C(2)–Ru–C(6)	106.9(1)
P(1)–Ru–O(5)	82.0(1)	P(2)–Ru–O(5)	171.3(1)
P(1)–Ru–P(2)	105.5(1)		
Ru–C(1)–C(2)	73.6(2)	Ru–C(5)–C(6)	72.5(3)
Ru–C(2)–C(1)	68.7(2)	Ru–C(6)–C(5)	68.9(3)
C(1)–C(2)–C(3)	123.1(3)	C(5)–C(6)–C(7)	117.1(3)
C(2)–C(3)–O(1)	126.4(4)	C(6)–C(7)–O(4)	127.5(3)
C(2)–C(3)–O(2)	112.1(4)	C(6)–C(7)–O(3)	112.9(4)
O(1)–C(3)–O(2)	121.4(5)	O(4)–C(7)–O(3)	119.6(4)
C(3)–O(2)–C(4)	115.8(4)	C(7)–O(3)–C(8)	113.5(3)
O(4)–O(5)–O(1)	91.9(2)	H(5A)–O(5)–H(5B)	92.0(2)

TABLE 3. Atomic coordinates ($\cdot 10^4$) and equivalent isotropic displacement factors ($\text{pm} \cdot 10^8$) for **2aq**

	x	y	z	U_{eq}
Ru	3691(1)	1803(1)	3468(1)	139(2)
P(1)	4217(1)	3170(1)	3941(1)	150(4)
P(2)	3452(1)	2105(1)	2250(1)	146(4)
O(1)	3680(1)	-1394(3)	4348(2)	341(13)
O(2)	3238(1)	-2034(3)	3301(2)	377(14)
O(3)	2868(1)	920(3)	3766(2)	302(12)
O(4)	3303(1)	1974(3)	4687(2)	282(12)
O(5)	3887(1)	1191(3)	4611(1)	217(11)
C(1)	3979(1)	-21(4)	3441(2)	199(15)
C(2)	3634(1)	-470(4)	3224(2)	191(15)
C(3)	3527(1)	-1302(4)	3684(2)	270(18)
C(4)	3110(2)	-2874(6)	3718(3)	538(28)
C(5)	3458(1)	3607(5)	3696(2)	197(15)
C(6)	3207(1)	2501(4)	3479(2)	222(15)
C(7)	3144(1)	1819(4)	4037(2)	213(16)
C(8)	2804(1)	216(5)	4319(3)	388(20)
C(9)	4264(1)	4022(2)	4796(1)	165(14)
C(10)	4376	3214	5424	196(15)
C(11)	4380	3785	6052	234(15)
C(12)	4272	5164	6052	287(17)
C(13)	4159	5972	5424	287(17)
C(14)	4155	5401	4797	221(15)
C(15)	4645(1)	2298(3)	4235(1)	168(14)
C(16)	4924	2605	4896	203(15)
C(17)	5246	1979	5079	260(16)
C(18)	5287	1045	4601	272(16)
C(19)	5008	738	3939	262(16)
C(20)	4686	1364	3756	220(15)
C(21)	4282(1)	4679(2)	3446(1)	181(14)
C(22)	3999	5543	3056	205(14)
C(23)	4042	6747	2718	235(16)
C(24)	4368	7087	2771	244(16)
C(25)	4651	6223	3162	256(16)
C(26)	4608	5018	3499	223(15)
C(27)	3339(1)	3843(3)	1784(1)	208(14)
C(28)	3122	4717	1946	274(16)
C(29)	3028	6029	1616	367(18)
C(30)	3150	6466	1124	374(19)
C(31)	3367	5592	961	348(18)
C(32)	3461	4280	1291	264(15)
C(33)	3019(1)	1255(3)	1716(1)	189(14)
C(34)	2875	357	2046	204(14)
C(35)	2564	-329	1630	249(16)
C(36)	2396	-119	884	243(15)
C(37)	2540	779	553	247(15)
C(38)	2852	1466	970	205(15)

Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor. Atoms C(9)–C(38), which are in rigid groups, have standard deviations only for the pivot atom.

double bonds are slightly offset towards the terminal carbons.

As can be seen in Figs. 2 and 3, the two methyl acrylate molecules are oriented in an almost mirror-like fashion. They are fixed in this position by the water molecule through hydrogen bonds to the carbonyl oxygen atoms O(1) and O(4). The hydrogen atoms of this

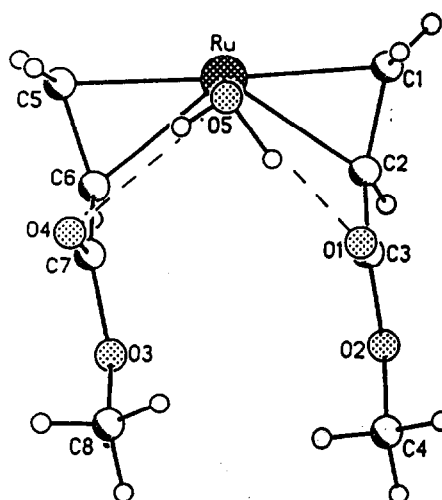


Fig. 2. Partial molecular structure of **2aq**, view perpendicular to the O(4)–O(5)–O(1) plane.

water molecule are located almost on the corresponding axes O(5)–O(1) (259.4 pm) and O(5)–O(4) (268.2 pm). These O–O distances are comparable to those observed in the acetic acid dimer (263.1 pm) [16]. Owing to this coordination the H–O–H bond angle is reduced to 92.0° and adjusts to the O(1)–O(5)–O(4) angle (91.9°).

Except for the extra H_2O ligand the molecular structure of **2aq** is comparable with that of bis(styrene)bis(triphenylphosphane)ruthenium [10]. However, because of the lack of structure "fixation" by a H_2O molecule $\text{Ru}(\text{C}_8\text{H}_8)_2(\text{PPh}_3)_2$ has a highly distorted tetrahedral geometry. The arrangement of the triphenylphosphane ligands is similar to that in **2aq** ($\text{Ru}(\text{P}1)_{\text{axial}}$ 241.1 pm; $\text{Ru}(\text{P}2)$ 221.6 pm; $\text{P}(1)\text{--Ru}(\text{P}2) = 107.8^\circ\text{C}$).

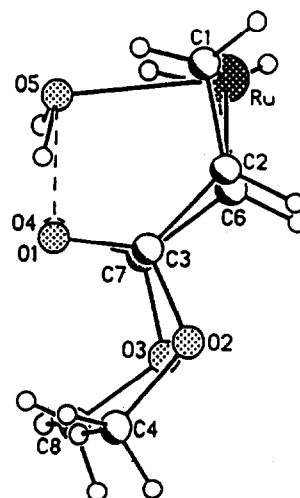


Fig. 3. Partial molecular structure of **2aq**, view along the O(4)–O(5)–O(1) plane.

2.2. NMR study of $Ru(MA)_2(PPh_3)_2(H_2O)$ (**2aq**)

The red crystals of **2aq** used for the X-ray analysis were also investigated by NMR spectroscopy in CD_2Cl_2 . The proton-decoupled ^{31}P NMR spectrum of the complex **2aq** at $-40^\circ C$ indicates the presence of two isomeric complexes I and II in a 65 : 35 ratio (Table 4). The rather narrow lines and the P,P-coupling constants (I: $J(P,P) = 15.5$ Hz, II: $J(P,P) = 16.5$ Hz) revealed that fast exchange of the phosphane ligands within each complex does not occur on the ^{31}P NMR time scale. When the NMR probe is warmed to $20^\circ C$ the signals broaden, especially so for the low-field phosphorus signals. The intensity ratio for the resonances of the two complexes does not change significantly. No dissociation of the complex, with release of triphenylphosphane ligands, occurs.

The phosphorus-decoupled 1H NMR spectrum as well as the ^{13}C NMR spectrum (Table 4) show three sets of signals for the methyl acrylate ligands. The assignment of the protons and the carbon atoms to each methyl acrylate results from $^1H, ^1H$ -COSY and $^1H, ^{13}C$ -COSY spectra. Owing to complexation the signals of the olefinic protons and carbon atoms are shifted by about 2 and 80 ppm, respectively, to higher field compared with those for free methyl acrylate. No dissociation of methyl acrylate was observed. Isomer I contains two equivalent methyl acrylate ligands, indicating a high symmetry for the complex. For isomer II two non-equivalent methyl acrylate ligands are seen. Thus, the two isomers differ in the geometry around ruthenium. In both isomers the triphenylphosphane ligands adopt a *cis*-arrangement.

In the light of these observations we suggest that both isomeric complexes have a trigonal bipyramidal structure, with one axial and an equatorial phosphane ligand, respectively. Since there is a symmetrical ar-

TABLE 4. $^1H(^{31}P)$ -, ^{13}C -, $^{31}P\{^1H\}$ NMR data for **2aq** at $-40^\circ C$ in CD_2Cl_2 ^a

	isomer I	isomer II	
$^{31}P\{^1H\}$	63.9 (d, $J(P,P) = 15.5$ Hz) 42.7 (d, $J(P,P) = 15.5$ Hz)	63.5 (d, $J(P,P) = 16.5$ Hz)	40.7 (d, $J(P,P) = 16.5$ Hz)
$^1H(^{31}P)$	3.64 (s, OCH_3) 3.26 (dd, CH, H_α) ^a 2.09 (dd, CH_2 , H_β^{cis}) ^a 1.91 (dd, CH_2 , H_β^{trans}) ^a 2.97 (s, H_2O)	3.72 (s, OCH_3) 3.18 (t, CH) ^c 1.76 (t, CH_2) ^c 1.61 (dt, CH_2) ^c	3.53 (s, OCH_3) 3.05 (m, CH') ^c 2.87 (m, CH_2') ^c 1.88 (m, CH_2') ^c
^{13}C	180.9 (C=O) 51.9 (CH_3) 44.4 (CH_2) 38.3 (CH)	184.2 (C=O) 51.5 (CH_3) 48.8 (CH_2) 37.0 (C'H)	181.7 (C'=O) 51.4 (C'H ₃) 40.7 (C'H ₂) 34.3 (CH)

^a Signals of PPh_3 at 7.4–6.3 ppm (1H NMR) and 137–125 ppm (^{13}C NMR) are omitted. ^b $J(H_\alpha, H_\beta^{trans}) = 9.72$ Hz, $J(H_\alpha, H_\beta^{cis}) = 7.64$ Hz, $J(H_\beta^{trans}, H_\beta^{cis}) = 2.91$ Hz. ^c Not completely resolved.

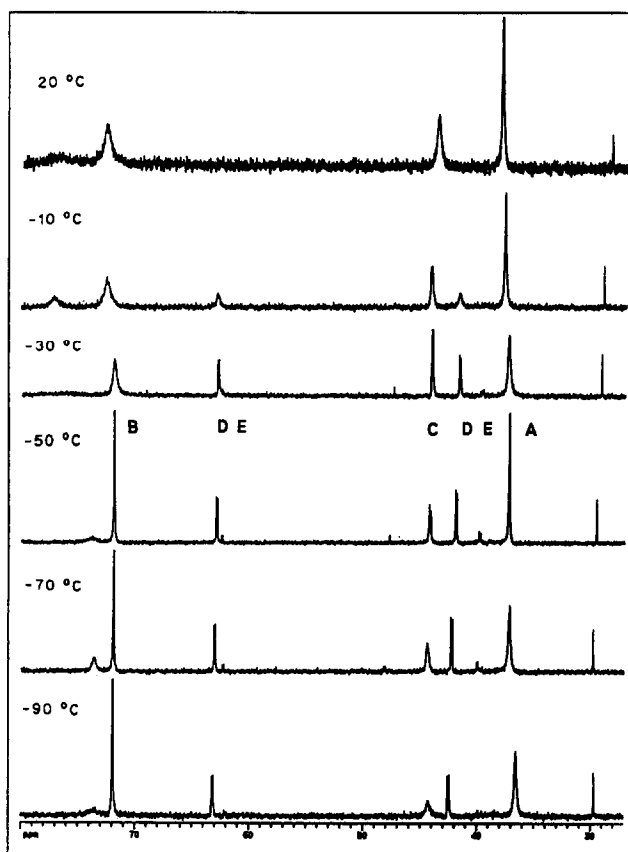


Fig. 4. Temperature dependency of the $^{31}P\{^1H\}$ NMR spectra of $Ru(MA)_2(PPh_3)_2$ (**2**) in CD_2Cl_2 .

angement of the methyl acrylate ligands in isomer I a structure similar to that revealed by the X-ray study can be assumed. In the case of isomer II the two methyl acrylate molecules are inequivalent; we suggest that the isomeric complex II contains an axial and an equatorial coordinated methyl acrylate ligand, with the water molecule in an equatorial position.

2.3. NMR study of $Ru(MA)_2(PPh_3)_2$ (**2**)

The yellow complex **2** was investigated by NMR spectroscopy in CD_2Cl_2 . The 1H NMR and ^{31}P NMR (Fig. 4) spectra are highly temperature dependent ($+20$ to $-90^\circ C$), pointing to dynamic behaviour of the complex. Line broadening was observed for the various resonances in the temperature range from $20^\circ C$ to $-90^\circ C$, indicating the operation of several exchange processes. In the temperature range from $-30^\circ C$ to $-50^\circ C$ a slowing of the exchange processes is observed. The sharpest lines were observed at $-40^\circ C$ (not shown in Fig. 4).

The 1H NMR spectra show a ratio of 30 aromatic to 12 aliphatic protons. Over the whole temperature range there is no evidence for the presence of a hydride species, such as that found by Komiya *et al.* [12] for the

TABLE 5. ^1H (^{31}P)-NMR-, ^{13}C -NMR- and ^{31}P -NMR-Data (ppm) for $\text{Ru}(\text{MA})_2(\text{PPh}_3)_2$ (**2**) at -40°C in CD_2Cl_2 (without signals of PPh_3)

	CH_3	CH_2	CH	rel. ratio (%)	$^{31}\text{P}/\text{PPh}_3$	rel. ratio (%)
A	^1H 2.70 (s)	1.28 (bs) 1.53 (d)	3.90 (t)	37	37.2 (s)	37
	^{13}C 49.5	39.2	45.6			
B	^1H 3.83 (bs)	2.26 (bd) 2.70	2.28 (bt)	37	71.8 (s)	37
	^{13}C 51.8	39.2	44.9			
C	^1H 3.65 (s)	1.78 (bs) 2.58 (d)	3.16 (bs)	18	43.9 (s) 44.0 (s)	18
	^{13}C 51.6	43.7	42.6			
D	^1H 3.70 (s)	1.91 (dd) $J = 2.8; 9.7$ 2.14 (dd) $J = 2.8; 7.6$	3.30 (t)	8	62.7 (d) 41.5 (d)	8
	^{13}C 50.8	44.5	38.5		$J = 15.5$	

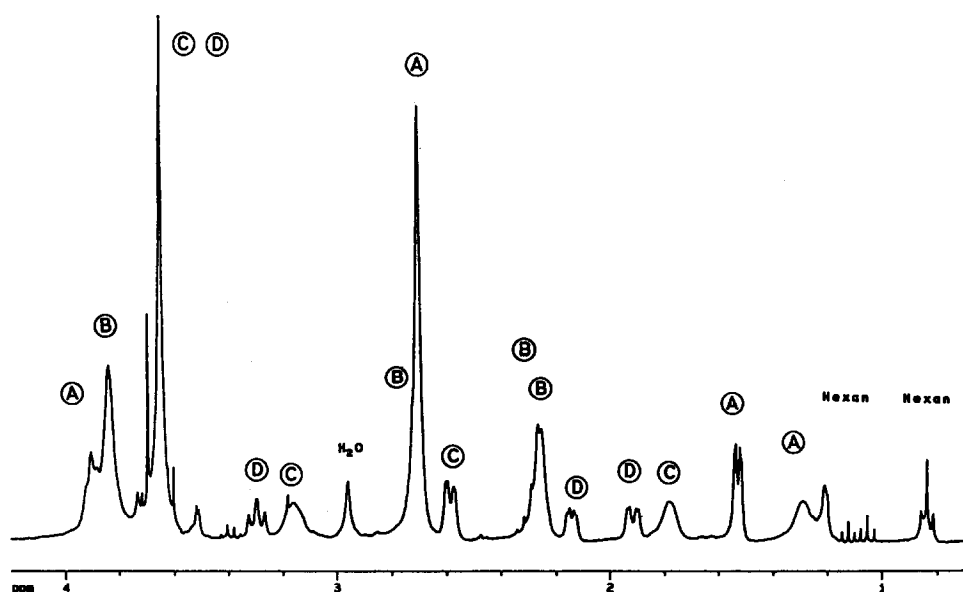
methyl methacrylate ruthenium complex. No dissociation of the complex, with release of methyl acrylate or phosphane ligands was observed. Therefore, the dynamic behaviour must be associated with intra-molecular exchange processes in $\text{Ru}(\text{MA})_2(\text{PPh}_3)_2$.

At -40°C the phosphorus-decoupled ^1H NMR and the ^{13}C NMR spectra display four sets of signals (Fig. 5, A–D) for the methyl acrylate molecules. In order to assign the proton signals to a particular methyl acrylate ligand the ^1H , ^1H -COSY, ^1H , ^{13}C -COSY and ^{13}C -NMR-DEPT spectra were recorded. The assignment is shown in Table 5.

The ^1H NMR spectrum exhibits a sharp singlet at

2.7 ppm assigned to the hydrogen atoms of a methoxy-carbonyl group. This high field shift (Δ 1.0 ppm) can only be explained by coordination of the carbonyl group to ruthenium. Because of the coordination of the carbonyl oxygen the ruthenium atom contains 18 valence electrons. The coordination scheme can be described as an “end on” coordination through the lone-pair of the carbonyl oxygen atom along with a η^4 - 4π coordination in which the ester molecule is bonded as an 1-oxabutadiene ligand (**2b**). Similar η^4 - 4π -coordination has been reported by Kuck and Knoll [17], who isolated an iron(0) complex with a η^4 -coordinated methyl methacrylate ligand forming an 1-oxabutadiene moiety. The signal of the methoxy protons of (η^4 -MMA) $\text{Fe}(\text{PF}_3)_3$ are shifted upfield (Δ 1.25 ppm) relative to that for free methyl methacrylate (MMA). The methoxy protons of the η^2 -coordinated methyl acrylate of (η^2 -MA) $\text{Fe}(\text{PF}_3)_4$ show no significant change in the chemical shift [17]. Because of this type of coordination the hydrogen atom of the methine group resonates at lower field (3.8 ppm) and the protons of the methylene group at higher field (1.53, 1.28 ppm) (set A, Fig. 5), relative to the resonances of the other methyl acrylate ligands (B, C, D). A comparable high-field shift for the methylene protons was found for (η^4 -MMA) $\text{Fe}(\text{PF}_3)_3$ [18].

If one methyl acrylate molecule is bonded as 1-oxabutadiene ligand the second MA must be η^2 -coordinated. Thus, the two ester ligands of one complex are non-equivalent. Therefore, data sets A and B, which have the same intensity, belong to the same complex. Owing to the η^4 - 4π -coordination of one methyl acrylate ligand the resonances of the methine proton and

Fig. 5. Partial ^1H (^{31}P) NMR spectrum of $\text{Ru}(\text{MA})_2(\text{PPh}_3)_2$ (**2**) in CD_2Cl_2 at -40°C .

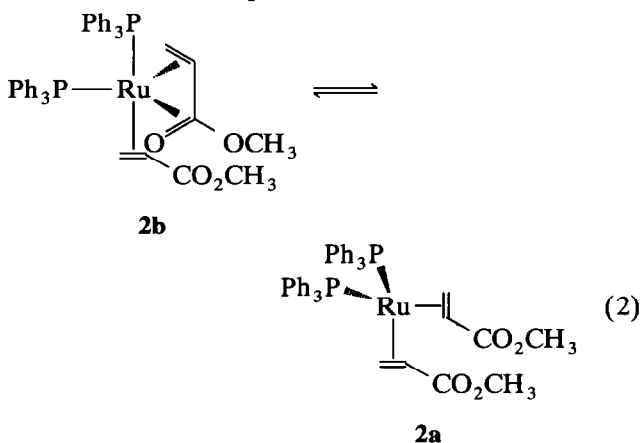
the methylene protons of the η^2 -coordinated methyl acrylate molecule are shifted in the opposite direction compared with data set A. The protons of the methine group now resonate at higher field (2.28 ppm) and the protons of the methylene group at lower field (2.26, 2.70 ppm) (set B, Fig. 5).

The ^{31}P NMR spectrum at -40°C (comparable to the spectra at -30°C and -50°C shown in Fig. 4) displays two broad singlets, at 37.2 and 71.8 ppm, with the intensities corresponding to the ^1H NMR signal intensities of data sets A and B. On the assumption of a trigonal bipyramidal geometry for the complex, the high field singlet can be attributed to an axially oriented triphenylphosphane ligand and the low field signal to an equatorially bonded one. At -40°C the structure of $\text{Ru}(\text{MA})_2(\text{PPh}_3)_2$ can be described as $(\eta^4\text{-2-methoxy-1-oxabutadiene})(\eta^2\text{-methylacrylate})\text{bis}(\text{triphenylphosphane})\text{-ruthenium}(0)$ (**2b**). This complex amounts to about 74% of the equilibrium mixture.

Complex **2b** would be expected to convert easily into an isomer **2a** having two η^2 -bonded methyl acrylate ligands, because an ester group has only a low tendency to coordinate to metals in the oxidation state zero [18]. The ^{31}P NMR spectrum shows two singlets (Fig. 4, C), at 43.9 and 44.0 ppm, indicating an isomer with low distortion of the symmetry. From the observed signal intensities the data set C for the methyl acrylate ligands can be assigned to isomer **2a**. Because of the two nearly equivalent triphenylphosphane and the two equivalent η^2 -bonded methyl acrylate ligands, a tetrahedral structure can be proposed for **2a**. The equilibrium concentration is 18%.

The data set D corresponds to the isomer I of **2aq**, the mono-aqua adduct (8%). Isomer II of this complex is detectable in the ^{31}P NMR spectrum (Fig. 5, E) only in traces.

The temperature-dependent exchange processes, which are completely reversible, involve the equilibrium between η^2 - (**2a**) and η^4 -coordinated methyl acrylate (**2b**) [eqn. (2)]. These exchange processes can not be frozen out at temperatures as low as -90°C .



The addition of 1 equiv of H_2O to the solution of $\text{Ru}(\text{MA})_2(\text{PPh}_3)_2$ (**2**) in CD_2Cl_2 gives $\text{Ru}(\text{MA})_2(\text{PPh}_3)_2(\text{H}_2\text{O})$ (**2aq**) in quantitative yield. The NMR spectra are identical to those of $\text{Ru}(\text{MA})_2(\text{PPh}_3)_2(\text{H}_2\text{O})$ (**2aq**) and also show the same ratio of the isomers I and II (66%:34%). Further addition of water does not change the spectra.

2.4. Infrared spectrum of $\text{Ru}(\text{MA})_2(\text{PPh}_3)_2$ (**2**)

The NMR spectra indicate that $\text{Ru}(\text{MA})_2(\text{PPh}_3)_2$ (**2**) mainly contains one $\eta^4\text{-}4\pi$ - and one $\eta^2\text{-}2\pi$ -coordinated methyl acrylate ligand, in solution at -40°C . Because of the air-stability of the solid and the yellow colour, an 18 valence electron complex can be proposed.

The infrared spectrum of solid **2** shows no evidence for the presence of a ruthenium hydride. In the characteristic frequency range of $2100\text{--}1700\text{ cm}^{-1}$ for such a species only the aromatic overtone bands are visible. An *ortho*-metallated phosphane ligand can also be excluded because of the absence of their typical bands [20] at 1552 and 1414 cm^{-1} . The ester carbonyl stretching frequency, which appears at 1725 cm^{-1} in free methyl acrylate, exhibits a 23 cm^{-1} shift to lower frequencies on complexation. If a η^4 -coordination of the second methyl acrylate is assumed, the band at 1391 or 1371 cm^{-1} , respectively, may be assigned to the stretching frequency of the π -bonded carbonyl group. This shift of about 300 cm^{-1} is comparable to that found for $(\eta^4\text{-MMA})\text{Fe}(\text{PF}_3)_3$ [17]. If the $\eta^4\text{-}4\pi$ -coordination of one methyl acrylate is accepted, the solid complex has 18 valence electrons and, hence, its description as $(\eta^2\text{-MA})(\eta^4\text{-MA})\text{Ru}(\text{PPh}_3)_2$ (**2b**) can be justified.

3. Conclusion

The reaction of $\text{H}_2\text{Ru}(\text{PPh}_3)_4$ (**1**) with methyl acrylate (MA) does not yield poly(methylacrylate) [4] but gives the new ruthenium olefin complex bis(methylacrylate)bis(triphenylphosphane)ruthenium(0) (**2**). This complex contains two differently coordinated methyl acrylate ligands in solution (and probably also in the solid state). Addition of water induces a change of the $\eta^4\text{-}4\pi$ -coordination of methyl acrylate to a $\eta^2\text{-}2\pi$ -coordination, in which the coordinated ester carbonyl group is replaced by a water molecule to give the mono-aqua adduct **2aq**.

4. Experimental details

All manipulations were carried out under dry argon using standard Schlenk tube techniques. The solvents were thoroughly degassed and dried over sodium ben-

zophenone ketyl(toluene), LiAlH_4 (n-hexane), CaH_2 (methyl acrylate) and molecular sieves (CD_2Cl_2), respectively. Infrared spectra were recorded on a Perkin-Elmer FT 1600. ^1H , $^1\text{H}\{^{31}\text{P}\}$, ^{31}P , and ^{13}C NMR spectra were recorded on a Bruker AMX 300. Assignment of the various resonances was achieved by ^1H , $^1\text{H}\text{-COSY}$ and ^1H , $^{13}\text{C}\text{-COSY}$, $^1\text{H}\{^{31}\text{P}\}$, and ^{31}C (BB, DEPT 135, DEPT 90) spectra. Microanalyses were performed on a Carlo Erba Elemental Analyzer Mod 1106. $\text{H}_2\text{Ru}(\text{PPh}_3)_4$ was prepared as previously described [19].

4.1. Bis(methylacrylate)bis(triphenylphosphane)ruthenium(0) 2

Addition of 10 ml (110 mmol) methyl acrylate to 1.52 g (1.32 mmol) of $\text{H}_2\text{Ru}(\text{PPh}_3)_4$ yielded a deep red solution. Evaporation *in vacuo* to dryness left a red, resin-like solid. This was stirred with n-hexane (25 ml) to remove liberated triphenylphosphane, leaving a fine yellow solid. After filtration (G4-frit) and repeated washing with n-hexane, the yellow solid was dried *in vacuo* (66 Pa). Yield 0.860 g (1.08 mmol, 82%), mp(dec.): 105–107°C.

Elemental analysis: $\text{C}_{44}\text{H}_{42}\text{O}_4\text{P}_2\text{Ru}$ (797.83); calc.: C, 66.24; H, 5.31; found: C, 66.18(± 0.22); H, 5.26(± 0.13)%.

IR (KBr): 3062 ($\nu(\text{CH}_{\text{arom}}$), m), 3048 ($\nu(\text{CH}_{\text{arom}}$), m), 2951 ($\nu(\text{CH}_{\text{aliph}}$), m), 1968w, 1918w, 1844w, 1702 ($\nu(\text{CO})$, s), 1654 ($\nu(\text{C}=\text{C}_{\text{arom}}$), w) 1532 ($\nu(\text{C}=\text{C}_{\text{coord}}$), m), 1418 ($\nu(\text{P}-\text{Ph})$, m), 1452 ($\nu(\text{C}=\text{C}_{\text{coord}}$), s), 1433 ($\nu(\text{P}-\text{Ph})$, s), 1391 ($\nu(\text{C}=\text{O}_{\text{coord}}$), s), 1370 ($\nu(\text{C}=\text{O}_{\text{coord}}$), s), 1230s, 1189m, 1148s, 1086m, 999m, 990m, 860w, 745 ($\delta(\text{CH}_{\text{arom}}$), m), 696 ($\delta(\text{CH}_{\text{arom}}$), s), 543m, 522s, 490m; (? indicates possible assignments).

4.2. X-ray structure analysis

A single crystal of the approximate dimension $0.37 \times 0.22 \times 0.19 \text{ mm}^3$ was sealed in a capillary and data were collected on an R3-mV-four-circle diffractometer (Nicolet) with graphite monochromatized Mo $\text{K}\alpha$ radiation ($\lambda = 710.69 \text{ pm}$) at 120 K. The cell dimensions were refined from the diffractometer angles of 50 reflections in the range of $20 \leq 2\theta \leq 25$, $a = 4293.9(7)$, $b = 953.0(2)$, $c = 2056.9(3) \text{ pm}$, $\beta = 116.01(1)^\circ$, $Z = 8$, $d_{\text{calc}} = 1.405 \text{ g cm}^{-3}$, $\mu = 0.54 \text{ mm}^{-1}$ monoclinic symmetry, space group $C2/c$. 5571 independent ($2\theta_{\text{max}} 45^\circ$) and 4908 observed intensities ($F_o \geq 4\sigma(F)$) were used for the structure solution by Patterson methods and refinement with full matrix least squares (SHELXTL-PLUS [20]) of 433 parameters resulting in $R_F = \Sigma(|F_o| - |F_c|) / \Sigma|F_c| = 0.0479$, $R_w(F) = \{\Sigma[w \cdot$

$(|F_o| - |F_c|)^2] / \Sigma w |F_o|^2\}^{0.5} = 0.0543$, $w^{-1} = (\sigma^2(F_o) + 0.00345(F_o)^2)$, with all non-hydrogen atoms given anisotropic temperature parameters, rigid models assigned to phenyl and methyl groups, unique isotropic temperature parameters used for each group of hydrogen atoms, and the oxygen-bonded hydrogen atoms freely refined. The maximum residual electron density was $0.481 \text{ e/pm}^3 \cdot 10^6$ and the minimum $-0.422 \text{ e/pm}^3 \cdot 10^6$ [21*].

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* Reference number with asterisk indicates a note in the list of references.