

Ruthenium carbonyl carboxylates with nitrogen containing ligands: IV. Catalytic activity in the hydroformylation of olefins in homogeneous phase¹

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Abstract

Ruthenium carbonyl acetato complexes containing bipyridines or phenantrolines ligands are tested as catalysts in the hydroformylation of hex-1-ene in homogeneous phase. These catalysts are active also in solutions containing water and the selectivity to aldehyde is high. Only a moderate hydrogenation of the alkene occurs. The regioselectivity to the linear aldehyde reaches 85.7% when using the mononuclear complex containing 4,7-dmphe as ligand. In the course of the reaction the starting olefin is largely isomerized. © 1997 Elsevier Science S.A.

1. Introduction

The hydroformylation of olefins is an industrial process used to manufacture commodities and specialities [2]. The most active catalysts are Rh and Co based, however ruthenium complexes too [3–5], show a moderate catalytic activity.

In recent years, in connection with the problems due to waste disposal and security on the plant, attempts have been done to reduce the use of organic solvents by replacing them with water or solvent-water mixtures. The most encouraging results in the hydroformylation were obtained by using catalysts containing sulphonated phosphines as ligands [6]. This kind of phosphine is valuable in the hydroformylation of propene, but several problems arise when higher olefins are hydroformylated [2]. Furthermore the use of phosphine ligands has some problems due to the stability and toxicity of these ligands. We have tried to overcome these problems by using nitrogen containing ligands such as bipyridines or phenantrolines, in consideration of their stability in the reaction conditions used for hydrogenation [1]. Several ruthenium carbonyl acetato complexes of the type $[Ru(CO)_2(MeCO_2)_2(N-N)]$ and $[Ru_2(CO)_4(MeCO_2)(N-N)_2(X)]$ have been prepared

[7,8] and tested as hydrogenation catalysts [1]. We have now extended the use of these complexes as catalytic precursors in the hydroformylation of a representative olefin like hex-1-ene in a water containing solvent.

Pakkanen et al. [9–12] reported the use of supported and unsupported ruthenium complexes containing bipyridine ligands as catalysts in the hydroformylation of hex-1-ene to the corresponding alcohols but they used different catalytic precursors and, mainly, supported catalysts.

Very recently Mitsudo et al. [13] have reported the use of $Ru_3(CO)_{12}/1,10$ -phenanthroline in the hydroformylation of several α -olefins, using an amide solvent to obtain aldehydes in high yields.

2. Results

The results of the hydroformylation of hex-1-ene in the presence of the ruthenium carbonyl carboxylato complexes with nitrogen containing ligands are reported in Tables 1 and 2. The solvent used in these experiments, in homogeneous phase, is a tetrahydrofuran-water (30:5) solution.

The reaction products of the hydroformylation carried out at 150°C under a carbon monoxide/hydrogen (1:1) pressure of 100 atm, are heptanal and 2-methylhexanal, the linear aldehyde being the prevailing iso-

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¹ For part III see Ref. [1].

Table 1
Hydroformylation of hex-1-ene in the presence of ruthenium carbonyl carboxylates with nitrogen containing ligand

Catalytic precursor	Hydroformylation yield (%)	TOF ^a (h ⁻¹)	Heptanal (%)	2-Methylhexanal (%)	Hexane (%)	Residual olefins (%)	Heptanal/total aldehydes (%)
[Ru ₂ (CO) ₂ (MeCO ₂) ₂ (bip) ₂](MeCO ₂)	25.6	10.7	20.1	5.5	1.6	72.8	78.5
[Ru ₂ (CO) ₂ (MeCO ₂) ₂ (4,4'-dmbip) ₂](MeCO ₂)	23.9	10.0	18.9	5.0	2.5	73.6	79.1
[Ru ₂ (CO) ₂ (MeCO ₂) ₂ (phen) ₂](MeCO ₂)	6.1	2.5	5.0	1.1	1.8	92.1	82.0
[Ru ₂ (CO) ₂ (MeCO ₂) ₂ (4,7-dmphen) ₂](MeCO ₂)	7.1	3.0	5.8	1.3	2.5	90.4	81.7
[Ru ₂ (CO) ₂ (MeCO ₂) ₂ (5,6-dmphen) ₂](MeCO ₂)	33.7	14.0	25.6	8.1	1.5	64.8	76.0
[Ru ₂ (CO) ₂ (MeCO ₂) ₂ (bip) ₂](BPh ₄)	23.4	9.8	18.8	4.6	1.9	74.7	80.3
[Ru ₂ (CO) ₂ (MeCO ₂) ₂ (4,4'-dmbip) ₂](BPh ₄)	9.3	3.9	7.5	1.7	2.9	87.9	81.5
[Ru ₂ (CO) ₂ (MeCO ₂) ₂ (phen) ₂](BPh ₄)	33.8	14.1	24.9	8.9	1.3	64.9	73.7
[Ru ₂ (CO) ₂ (MeCO ₂) ₂ (4,7-dmphen) ₂](BPh ₄)	6.7	2.8	5.6	1.1	2.1	91.2	83.6
[Ru ₂ (CO) ₂ (MeCO ₂) ₂ (5,6-dmphen) ₂](BPh ₄)	7.5	3.1	6.2	1.3	2.3	90.2	82.7
Ru(CO) ₂ (MeCO ₂) ₂ (bip)	10.2	4.3	8.1	2.1	3.5	86.3	79.4
Ru(CO) ₂ (MeCO ₂) ₂ (4,4'-dmbip)	20.8	8.7	16.1	4.7	1.9	77.3	77.4
Ru(CO) ₂ (MeCO ₂) ₂ (phen)	8.0	3.3	6.3	1.7	2.9	89.1	78.8
Ru(CO) ₂ (MeCO ₂) ₂ (2,9-dmphen)	22.8	9.5	15.2	7.6	3.7	73.5	66.7
Ru(CO) ₂ (MeCO ₂) ₂ (4,7-dmphen)	11.2	4.7	9.6	1.6	5.1	83.7	85.7
Ru(CO) ₂ (MeCO ₂) ₂ (5,6-dmphen)	29.7	12.4	22.1	7.6	2.2	68.1	74.4

Substrate 17.51 mmol, catalyst 17.51 μ mmol-Ru, solvent: water 5 ml + tetrahydrofuran 30 ml, $p_{H_2} = 50$ atm at 20°C, $p_{CO} = 50$ atm at 20°C, $T = 150^\circ\text{C}$, reaction time 24 h.

^aTOF: turn over frequency (mol aldehyde)/(mol-Ru \times h).

mer. With all the complexes tested, 2-ethylpentanal is never formed even when the substrate is largely isomerized in the course of the reaction. The extent of the isomerization, as suggested by the amount of internal hexenes formed, is in fact higher than the hydroformylation whatever the catalytic precursor used. The mixture of the residual olefins, as it also happens when these complexes are used as catalysts in the hydrogenation of alkenes, contains *trans*-hex-2-ene as the main component while *cis*-hex-3-ene is the lowest (about 1.0% of the residual olefins). In the presence of Ru(II) complexes the residual olefin reaches 62.9% of the starting alkene when the catalyst is Ru(CO)₂(MeCO₂)₂(5,6-dmphen). In the presence of the catalyst containing an unsubstituted bipyridine or phenantroline ligand the amount of isomerized olefin is lower (22.5–20.5% respectively).

Binuclear Ru(I) complexes cause a fairly low contemporary hydrogenation of the substrate in spite of the relatively high temperature used (150°C): *n*-hexane never exceeds 2.9% of the starting substrate, whatever the complex used. With the mononuclear Ru(II) complexes the hydrogenation of hex-1-ene is slightly higher: up to 5.1% of the starting alkene.

The Ru(I) complexes containing bipyridine as ligand, have almost the same catalytic activity independently from the anion, acetato or tetraphenylborate. The same occurs when the ligand is 4,7-dmphen, even if the catalytic activity of these complexes is lower than that of the complexes containing bipyridine. A different behaviour has been observed using the ruthenium complexes of the type [Ru₂(CO)₂(MeCO₂)₂(N–N)₂(X), with

4,4'-dmbip or 5,6-dmphen as nitrogen containing ligand. The catalytic activity is reduced when the acetato is replaced by the tetraphenylborate anion: the yield decreases from 23.9 to 9.3% in the first case and from 33.7 to 7.5%, in the second one. An opposite behaviour, that is, an increase of the catalytic activity has been noticed with the same substitution of the anion when the N–N ligand is phenantroline: the yield increases from 6.1 to 33.8%.

The ratio between normal to branched aldehyde has the lowest value of 2.7 when using [Ru₂(CO)₂(MeCO₂)₂(phen)₂](BPh₄) and the highest of 5.1 with [Ru₂(CO)₂(MeCO₂)₂(4,7-dmphen)₂](BPh₄) as catalyst.

A perusal of the data from alkene hydroformylation tests performed using mononuclear ruthenium complexes of the type Ru(CO)₂(MeCO₂)₂(N–N) as catalytic precursors (Table 1) indicates that the presence of a methyl substituent on the bipyridine ligand increases the catalytic activity if compared to the corresponding complex containing unsubstituted bipyridine. An opposite behaviour is shown by the complexes containing phenantrolines as ligands. In this case the Ru(CO)₂(MeCO₂)₂(5,6-dmphen), Ru(CO)₂(MeCO₂)₂(2,9-dmphen) and Ru(CO)₂(MeCO₂)₂(4,4'-dmbip) complexes show a good activity (conversion into aldehydes of 29.7, 22.8 and 20.8% respectively, corresponding to a TOF of 12.4, 9.5 and 8.7 h⁻¹, respectively). The molar ratio between linear to branched aldehyde is generally in the range 2.9–3.9. Two exceptions are observed: with the complex containing the 2,9-dmphen ligand the lowest value

Table 2
Hydroformylation of hex-1-ene in the presence of ruthenium carbonyl carboxylates containing nitrogen ligands. Residual olefin composition (%)

Catalytic precursor	<i>trans</i> -Hex-2-ene (%)	<i>cis</i> -Hex-2-ene (%)	<i>trans</i> -Hex-3-ene (%)	<i>cis</i> -Hex-3-ene (%)	Hex-1-ene (%)	Olefin isomerization, yield (%)
$[\text{Ru}_2(\text{CO})_4(\text{MeCO}_2\text{Xbp})_2](\text{MeCO}_2)$	54.5	22.0	7.7	1.1	14.7	62.1
$[\text{Ru}_2(\text{CO})_4(\text{MeCO}_2\text{X}4,4\text{-dmbip})_2](\text{MeCO}_2)$	45.9	18.5	4.4	1.4	29.8	31.7
$[\text{Ru}_2(\text{CO})_4(\text{MeCO}_2\text{Xphen})_2](\text{MeCO}_2)$	8.5	2.7	1.1	1.3	86.4	12.5
$[\text{Ru}_2(\text{CO})_4(\text{MeCO}_2\text{X}4,7\text{-dimphen})_2](\text{MeCO}_2)$	10.4	3.3	0.7	1.2	84.4	14.1
$[\text{Ru}_2(\text{CO})_4(\text{MeCO}_2\text{X}5,6\text{-dimphen})_2](\text{MeCO}_2)$	56.4	22.4	12.0	1.5	7.7	59.8
$[\text{Ru}_2(\text{CO})_4(\text{MeCO}_2\text{Xbp})_2](\text{BPh}_4)$	44.2	15.5	3.6	1.5	35.2	48.4
$[\text{Ru}_2(\text{CO})_4(\text{MeCO}_2\text{X}4,4\text{-dmbip})_2](\text{BPh}_4)$	14.2	5.8	0.8	1.5	77.7	19.7
$[\text{Ru}_2(\text{CO})_4(\text{MeCO}_2\text{Xphen})_2](\text{BPh}_4)$	53.2	21.4	16.6	1.4	7.4	60.1
$[\text{Ru}_2(\text{CO})_4(\text{MeCO}_2\text{X}4,7\text{-dimphen})_2](\text{BPh}_4)$	11.5	3.8	0.7	1.1	82.9	15.7
$[\text{Ru}_2(\text{CO})_4(\text{MeCO}_2\text{X}5,6\text{-dimphen})_2](\text{BPh}_4)$	10.8	3.4	0.6	1.2	84.0	14.4
$[\text{Ru}(\text{CO})_2(\text{MeCO}_2)_2(\text{bp})]$	18.0	5.5	1.3	1.3	73.9	22.5
$[\text{Ru}(\text{CO})_2(\text{MeCO}_2)_2(4,4\text{-dmbip})]$	44.1	17.7	3.8	1.3	33.1	51.7
$[\text{Ru}(\text{CO})_2(\text{MeCO}_2)_2(\text{phen})]$	13.8	6.4	1.1	1.7	77.0	20.5
$[\text{Ru}(\text{CO})_2(\text{MeCO}_2)_2(2,9\text{-dimphen})]$	44.3	15.5	7.5	1.4	31.3	50.5
$[\text{Ru}(\text{CO})_2(\text{MeCO}_2)_2(4,7\text{-dimphen})]$	34.7	10.3	3.0	1.3	50.7	41.3
$[\text{Ru}(\text{CO})_2(\text{MeCO}_2)_2(5,6\text{-dimphen})]$	55.2	21.9	13.7	1.6	7.6	62.9

Substrate 17.51 mmol, catalyst 17.51 μmol -Ru, solvent: water 5 ml + tetrahydrofuran 30 ml, P_{H_2} = 50 atm at 20°C, p_{CO} = 50 atm at 20°C, T = 150°C, reaction time 24 h.

of 2.0 is obtained while using those containing 4,7-dmpphen the highest ratio of 6.0 is reached.

3. Conclusion

The complexes tested show a fair catalytic activity for the hydroformylation and isomerization of olefins in a water containing solvent. They provide however only aldehyde as hydroformylation products. These results are therefore different from those reported by Pakkanen, using supported ruthenium carbonyls/bipyridine system [9–11].

Our results are not very different from those reported by Mitsudo et al. [13]. Infact they obtain aldehydes with yields of ca. 50% and a selectivity with respect to *n*-aldehyde major than 95%.

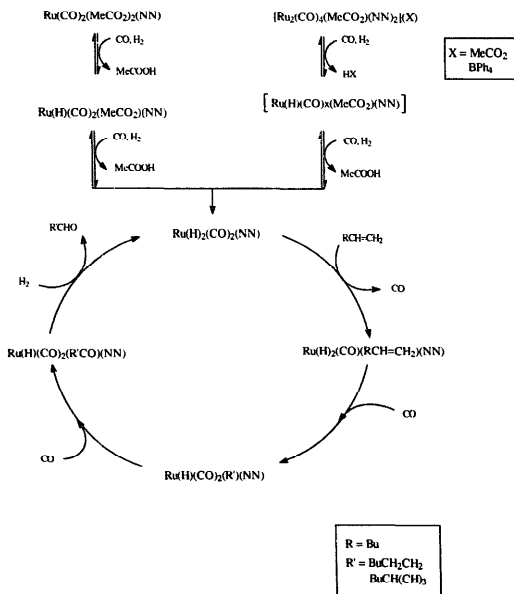
Alcohols are not observed among our reaction products. Since the same catalytic precursors are active in both the hydroformylation and the hydrogenation of olefins, when separately performed, the presence of carbon monoxide, during the hydroformylation reaction, changes the evolution of the alkyl species toward carbon monoxide insertion instead of the hydrogenolysis to

alkane. In fact, even when working at 150°C under hydroformylation conditions, the only hydrogenated product is hexane and it is formed in very low amount.

When using the mononuclear Ru(II) complexes the linear aldehyde is formed with a regioselectivity ranging from 66.7% with $\text{Ru}(\text{CO})_2(\text{MeCO}_2)_2(2,9\text{-dmpphen})$ to 85.7% with $\text{Ru}(\text{CO})_2(\text{MeCO}_2)_2(4,7\text{-dmpphen})$. With binuclear Ru(I) complexes the regioselectivity towards the linear aldehyde changes from 73.7% with $[\text{Ru}_2(\text{CO})_4(\text{MeCO}_2)(\text{phen})_2](\text{BPh}_4)$ to 83.6% with $[\text{Ru}_2(\text{CO})_4(\text{MeCO}_2)(4,7\text{-dmpphen})_2](\text{BPh}_4)$.

Almost the same selectivity provided by mononuclear and binuclear ruthenium complexes in the formation of aldehyde may suggest the formation of the same catalytic intermediate in both cases. An analogous behaviour was shown by the phosphine substituted ruthenium carbonyl carboxylates [14]: The carboxylato group, under CO and H_2 , was displaced and phosphine substituted Ru(0) carbonyl complexes were formed.

This hypothesis has been confirmed by reacting, separately, a Ru(I) or a Ru(II) complex, with CO and H_2 under hydroformylation conditions (150°C, 100 atm CO: H_2 1:1, reaction time 3 h). The IR spectra of the complexes recovered at the end of the reaction, in the



Scheme 1.

2200–1800 cm^{-1} region, were practically the same and did not indicate the presence of the carboxylato ligands.

Furthermore, treatment of $\text{Ru}(\text{CO})_2(\text{CH}_3\text{CO}_2)_2(5,6\text{-dmphen})$ with hydrogen alone gives rise to the formation of a hydride ruthenium complex as shown by the resonance at -25.0 ppm in the ^1H NMR spectrum [1]. A hypothesis to rationalise these results is reported in Scheme 1.

The mononuclear complexes react with CO and H_2 , the carboxylato group is displaced and a mononuclear ruthenium dihydrido complex with nitrogen containing ligand is formed. This is the catalytic complex that, in the presence of syn gas transforms the olefin into aldehydes.

The binuclear complexes are transformed in an analogous way, as it happens for the phosphine substituted complexes [14], into mononuclear dihydro derivatives with nitrogen containing ligand.

The different anions present in the catalytic precursors play a role in the formation of the catalytic species and therefore affect the yield of the reaction.

We can conclude that the main characteristic of these complexes is their ability to catalyse the hydroformylation and isomerization of olefins in a water containing medium.

4. Experimental

4.1. Apparatus and analytical methods

IR spectra were recorded with a FT-IR Perkin-Elmer model 1760 instrument using KBr or CaF_2 windows for solutions and KBr pellets for solid samples.

GC analyses were performed using a gc apparatus for packed columns Shimadzu mod. GC-14A with a computer Shimadzu C-R4A and a gc instrument for capillary columns Perkin-Elmer mod. 8320. All instrument had FID detectors. The following columns were used: a packed (2 m) PPG: Polypropyleneglicol LB-550-X 15% supported on Chromosorb W and a capillary column Al_2O_3 PLOT containing alumina (50 m, internal diameter 0.32 mm). Quantitative analyses of isomeric compounds were performed assuming that all products had the same response factors.

Gc-ms analyses were performed using a gc apparatus for capillary columns Shimadzu mod. GC-14A equipped with a capillary columns SPB-1TM (30 m, i.d. 0.25 mm) and a mass detector Shimadzu QP2000.

4.2. Materials

All preparations and manipulations were routinely performed under a dry nitrogen atmosphere using Schlenk tube techniques.

2,2'-Bipyridine (Fluka), 4,4'-Dimethyl-2,2'-bipyridine (Aldrich), 1,10-Phenanthroline (Merck), 2,9-Dimethyl-

1,10-phenanthroline (Aldrich), 4,7-Dimethyl-1,10-phenanthroline (Aldrich), 5,6-Dimethyl-1,10-phenanthroline (Aldrich). Sodium tetraphenylborate (RPE-ACS C. Erba). Triruthenium dodecacarbonyl (Aldrich). $[\text{Ru}_2(\text{CO})_4(\text{MeCO}_2)_2]_n$ [15], $[\text{Ru}_2(\text{CO})_4(\text{CH}_3\text{CO}_2)(\text{bip})_2](\text{CH}_3\text{CO}_2)_2$ [8], $[\text{Ru}_2(\text{CO})_4(\text{CH}_3\text{CO}_2)(4,4'\text{-dmbip})_2](\text{CH}_3\text{CO}_2)_2$ [8], $[\text{Ru}_2(\text{CO})_4(\text{CH}_3\text{CO}_2)(\text{phen})_2](\text{CH}_3\text{CO}_2)_2$ [8], $[\text{Ru}_2(\text{CO})_4(\text{CH}_3\text{CO}_2)(4,7\text{-dmphen})_2](\text{CH}_3\text{CO}_2)_2$ [8], $[\text{Ru}_2(\text{CO})_4(\text{CH}_3\text{CO}_2)(5,6\text{-dmphen})_2](\text{CH}_3\text{CO}_2)_2$ [8], $[\text{Ru}_2(\text{CO})_4(\text{CH}_3\text{CO}_2)(\text{bip})_2](\text{BPh}_4)_2$ [8], $[\text{Ru}_2(\text{CO})_4(\text{CH}_3\text{CO}_2)(4,4'\text{-dmbip})_2](\text{BPh}_4)_2$ [8], $[\text{Ru}_2(\text{CO})_4(\text{CH}_3\text{CO}_2)(\text{phen})_2](\text{BPh}_4)_2$ [8], $[\text{Ru}_2(\text{CO})_4(\text{CH}_3\text{CO}_2)(4,7\text{-dmphen})_2](\text{BPh}_4)_2$ [8], $[\text{Ru}_2(\text{CO})_4(\text{CH}_3\text{CO}_2)(5,6\text{-dmphen})_2](\text{BPh}_4)_2$ [8], $\text{Ru}(\text{CO})_2(\text{CH}_3\text{CO}_2)_2(2,9\text{-dmphen})$ [7], $\text{Ru}(\text{CO})_2(\text{CH}_3\text{CO}_2)_2(4,7\text{-dmphen})$ [7], $\text{Ru}(\text{CO})_2(\text{CH}_3\text{CO}_2)_2(4,4'\text{-dmbip})$ [7], $\text{Ru}(\text{CO})_2(\text{CH}_3\text{CO}_2)_2(\text{phen})$ [7], $\text{Ru}(\text{CO})_2(\text{CH}_3\text{CO}_2)_2(2,9\text{-dmphen})$ [7], $\text{Ru}(\text{CO})_2(\text{CH}_3\text{CO}_2)_2(4,7\text{-dmphen})$ [7], $\text{Ru}(\text{CO})_2(\text{CH}_3\text{CO}_2)_2(5,6\text{-dmphen})$ [7] were synthesised as reported.

Methanol: C. Erba product, purified by the Lund and Bjerrum method reported by Vogel [16]. *Tetrahydrofuran*: RPE C. Erba product (900 ml) dried by refluxing on LiAlH_4 (10 g). The product collected by fractional distillation on LiAlH_4 had b.p. 65°C . *Acetone*: RPE-ACS C. Erba product purified according to Vogel [17]. *Hex-1-ene*: The Aldrich product has been eluted through an Al_2O_3 column and rectified in a nitrogen atmosphere (purity 99.99%).

4.3. Catalytic hydroformylation experiments

In a stainless steel autoclave (150 ml), evacuated from air, the catalytic precursor, the solvent, the olefin (hex-1-ene), hydrogen and carbon monoxide at the prefixed pressure were introduced. The autoclave was then placed in a thermostatic oil bath set at the desired temperature ($\pm 1^\circ\text{C}$) and rocked for the prefixed time. The amount of catalytic precursor, solvent, substrate, hydrogen and carbon monoxide pressure and reaction temperature are reported in Table 1. At the end, the reactor was cooled, the gases vented out and the solution analysed by gc. The hydroformylation products were identified and quantitatively determined by gc analysis, using a PPG column heated at 35°C for 20 min then heated up to 100°C at a rate of $2^\circ\text{C}/\text{min}$ and kept at this temperature for 20 min. The residual hydrocarbon composition was determined by gc analysis, using the Al_2O_3 PLOT capillary column heated at 130°C for 25 min then heated up to 200°C at a rate of $30^\circ\text{C}/\text{min}$ and kept at this temperature for 54 min. The identity of the products was confirmed by gc–ms analysis [18].

4.4. Reactivity of ruthenium complexes under hydroformylation conditions

In a stainless steel autoclave (150 ml), evacuated from air, the catalytic precursor

$\text{Ru}(\text{CO})_2(\text{CH}_3\text{CO}_2)_2(5,6\text{-dmphen})$ (20 mg), THF (5 ml), hydrogen (50 atm) and carbon monoxide (50 atm) were introduced. The autoclave was then placed in a thermostatic oil bath and heated at 150°C for 3 h. At the end, the reactor was cooled and the gases vented out and the solution analysed by IR. In the 2200–1500 cm^{-1} region, the following absorptions were present: 2040 (s), 2013 (sh), 1991 (vs), 1779 (vs), 1727 (vs), 1643 (w), 1513 (m).

In the same conditions, using the same procedure $[\text{Ru}_2(\text{CO})_4(\text{CH}_3\text{CO}_2)_2(5,6\text{-dmphen})_2](\text{CH}_3\text{CO}_2)_2$, gave the following absorptions in the IR spectrum at the end of the reaction: 2040 (s), 1993 (vs), 1780 (m), 1727 (m), 1648 (m), 1514 (m).

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