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PHOSPHINE-SUBSTITUTED RUTHENIUM CARBONYL CARBOXYLATES

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Summary

The behaviour of the $[Ru_2(CO)_4(CH_3COO)_2]_n$/tributylphosphine/acetic acid system has been investigated as a function of reaction conditions and molar ratios of reactants. Tricyclohexylphosphine and triethylphosphite were also used as ligands and investigation was extended to the related oxalic, malonic, succinic, glutaric and adipic acid derivatives. These derivatives were isolated and characterized in view of their possible role as catalysts in the homogeneous hydrogenation of carboxylic acids in the presence of phosphine- or phosphite-substituted ruthenium carbonyl derivatives.

Introduction

A phosphine-substituted ruthenium carbonyl carboxylate has recently been isolated from the crude of the homogeneous hydrogenation of acetic acid in the presence of $H_4Ru_4(CO)_8(PBu_3)_4$ [1] (PBu_3 = tri-n-butylphosphine). The detection of this product in such a mixture suggests that catalytically active species for this reaction may reasonably be found among products of this type, and several ruthenium carbonyl carboxylates have been recently detected in the residues from such reactions [1].

In order to understand the role played by these complexes, if any, in catalysing this reaction we undertook the synthesis of phosphine-substituted ruthenium carbonyl carboxylates with different [P]/[Ru] ratios which are likely to be formed under the catalysed reaction conditions. (We intend later to investigate their catalytic activity.) We thus investigated the behaviour of the system formed by $[Ru_2(CO)_4(CH_3COO)_2]_n$ (I), PR_3 and acetic acid as a function of reaction conditions and of the molar ratios of the reactants.

This investigation was extended to the corresponding derivatives of bicarboxylic acids in view of their possible role in the hydrogenation of bicarboxylic acids in the presence of $H_4Ru_4(CO)_8(PBu_3)_4$ [1].

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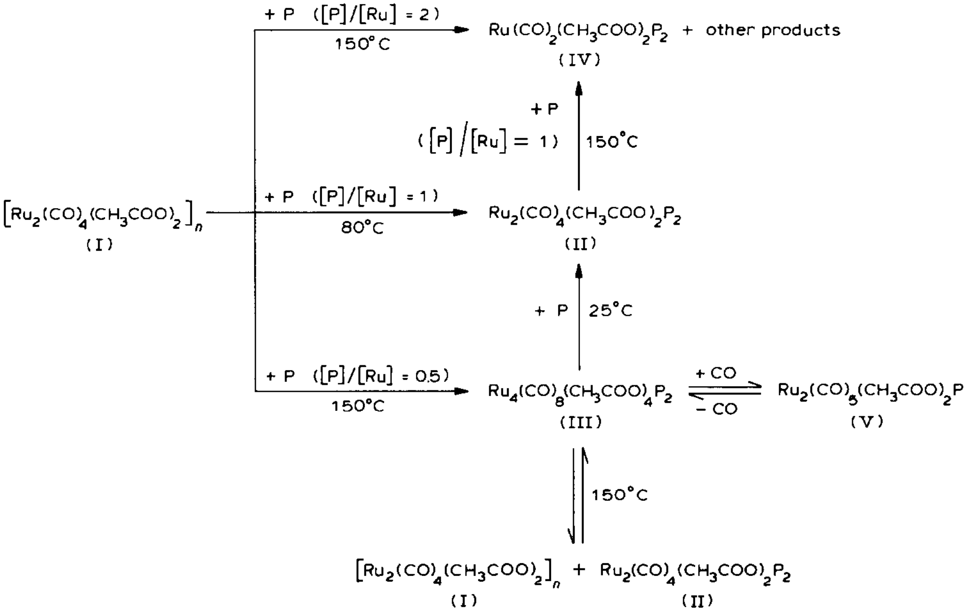
Results

In an earlier paper [2] we indicated that when I is treated with PBu_3 ([P]/[Ru] = 1), $Ru_2(CO)_4(CH_3COO)_2(PBu_3)_2$ (IIa) is formed (Scheme 1), as stated by Johnson et al. [3]. We also showed that $Ru_4(CO)_8(CH_3COO)_4(PBu_3)_2$ (IIIa) is formed by treating I with IIa, and that IIIa may also be directly obtained by treating I with PBu_3([P]/[Ru] = 0.5) in benzene at 150°C [2]. We have now found that IIa reacts with an excess of PBu_3 in benzene at 150°C to give $Ru(CO)_2(CH_3COO)_2(PBu_3)_2$ (IVa) in 30% yield; the low yield is due to deficiency of the acetato groups in the system; and if an excess of acetic acid is present the yield is raised to 70%. Complex IVa is also obtained from $Ru_3(CO)_{12}$ by reaction with PBu_3 to give $Ru(CO)_3(PBu_3)_2$ [4], followed by treatment of this compound with acetic acid, as suggested for the synthesis of $Ru(CO)_2(CH_3COO)_2(PPh_3)_2$ [5,6,7]. Complex IIIa is converted into $Ru_2(CO)_5(CH_3COO)_2(PBu_3)$ (Va) by addition of carbon monoxide even under very low carbon monoxide pressures. This reaction is readily reversed by heating Va at 50°C.



SCHEME 1. Solvent: benzene; IIa, IIIa, IVa, Va: P = PBu_3; IIb, IIIb: P = $P(OEt_3)$; IIc: P = PCy_3.

Triethylphosphite [$P(OEt)_3$] reacts with I to give only IIb and IIIb (Scheme 1). The lower reactivity and stability of this ligand [8] prevents the formation of products of further substitution. Reaction of I with tricyclohexylphosphine [PCy_3] gives only IIc.

$$Ru_3(CO)_{12} \xrightarrow{HOOC(CH_2)_mCOOH} \{Ru_2(CO)_4[OOC(CH_2)_mCOO]\}_n$$

$$\{Ru_2(CO)_4[OOC(CH_2)_mCOO]\}_n \xrightarrow{PBu_3} Ru_4(CO)_8[OOC(CH_2)_mCOO]_2(PBu_3)_4$$

SCHEME 2. $m = 0$–4.

Bicarboxylic acids (Scheme 2) react with $Ru_3(CO)_{12}$ to give the polymeric derivative $\{Ru_2(CO)_4[OOC(CH_2)_mCOO]\}_n$. This polymer reacts with PBu_3 to give $Ru_4(CO)_8[OOC(CH_2)_mCOO]_2(PBu_3)_4$. So far only derivatives of succinic and adipic acids have been obtained in pure form; the glutaric acid derivative has been previously described [2].

IR and NMR data of these new compounds are reported in Table 1.

Discussion

The reaction of I with phosphine is a depolymerization reaction, no evolution of carbon monoxide is observed. Whatever the [P]/[Ru] ratio, this reaction initially gives a binuclear repeating unit which includes two phosphine molecules, one for each ruthenium atom (Scheme 3).

$$[Ru_2(CO)_4(CH_3COO)_2]_n + 2\,PBu_3 \rightarrow$$

$$\underset{\text{(IIa)}}{Ru_2(CO)_4(CH_3COO)_2(PBu_3)_2} + [Ru_2(CO)_4(CH_3COO)_2]_{n-1}$$

SCHEME 3

Even in the presence of an excess of phosphine at temperatures below 150°C no more phosphine can be introduced into the molecule. At higher temperatures ($> 150°C$) the intermetallic bond in IIa is broken, with a change in the oxidation number of the metal. From the residue we have been able to isolate a mononuclear derivative of ruthenium containing two phosphine molecules (IVa), and no other species was identified containing ruthenium in the zero oxidation state.

The IR spectrum of IVa in the CO and COO stretching frequency region shows absorptions similar to those reported in the literature [6] for $Ru(CO)_2(CH_3COO)_2(PPh_3)_2$ (ν_{asym} 1622 cm^{-1}, ν_{sym} 1322 cm^{-1}, $\Delta\nu$ 300 cm^{-1}) characteristic for a monodentate carboxylate [9].

The IR spectra of derivatives of the type $Ru_2(CO)_4(RCOO)_2L_2$ (II) and of the corresponding polymeric precursor I show absorption bands in the region of the stretching frequencies of the COO group between 1585 and 1550 cm^{-1} and between 1440 and 1415 cm^{-1}, with $\Delta\nu$ in the range of 155–130 cm^{-1} indicative of the presence of a chelate carboxylic group bridging two ruthenium atoms [9].

Johnson and coworkers suggested for products such as $[Ru_2(CO)_4(CH_3COO)_2]_n$ a structure involving a metal–metal bond between atoms linked by bridging carboxylate groups [3]. Such a structure was confirmed by Schumann and Opitz by X-ray diffraction studies on $Ru_2(CO)_4(CH_3CH_2CH_2COO)_2\{P[C(CH_3)_3]_3\}$ [10,11]. The IR spectra of the succinic and adipic analogues of II show such close analogies with that of the glutaric derivative that the same structure must also be attributed to them.

Experimental

IR spectra were recorded with a Perkin–Elmer model 580 instrument; NMR spectra were recorded with a Perkin–Elmer R32 spectrometer; molecular weight determinations based on the isopiestic method were performed using a Wescam model 233 instrument.

(Continued on p. 212)

TABLE 1

IR AND NMR CHARACTERISTICS OF SOME RUTHENIUM CARBONYL CARBOXYLATES

	IR in the region 2200–1300 cm^{-1}		NMR (in C_6D_6) δ(TMS)
	ν(CO)	Other bands	
$[Ru_2(CO)_4(OOCCOO)]_n$ [a]	2030(vs), 1986(ms), 1940(vs), 1910(sh)	1639(s), 1407(w), 1325(s)	
$[Ru_2(CO)_4(OOCCH_2COO)]_n$ [a]	2040(vs), 1985(s), 1945(vs), 1910(sh)	1590(s), 1555(vw), 1450(m), 1430(vw), 1375(s)	
$[Ru_2(CO)_4(OOCCH_2CH_2COO)]_n$ [a]	2040(vs), 1990(s), 1960(vs), 1930(sh)	1578(s), 1438(s), 1420(sh), 1404(m), 1310(mw)	
$[Ru_2(CO)_4(OOCCH_2CH_2CH_2CH_2COO)]_n$ [a]	2034(vs), 1989(s), 1955(vs), 1942(sh)	1678(w), 1552(vs), 1453(sh), 1430(sh), 1410(s), 1319(mw), 1310(sh)	
$Ru(CO)_2(CH_3COO)_2(PBu_3)_2$ [b]	2028(vs), 2015(vw), 1972(vs), 1944(w)	1621(s), 1595(sh), 1462(m), 1455(sh), 1445(sh), 1418(w), 1363(s), 1314(s)	0.87(t, 18H, $\mathit{CH}_3(CH_2)_3P$), 1.10–2.00(m, 36H, $CH_3(\mathit{CH}_2)_3P$), 2.15 (s, 6H, CH_3COO)
$Ru_2(CO)_5(CH_3COO)_2(PBu_3)$ [b]	2072(s), 2059(sh), 2035(w), 2018(vs), 2005(sh), 1990(sh), 1979(vs), 1958(w), 1941(m)	1720(w), 1578(m), 1438(m), 1380(vw), 1347(vw)	0.85(t, 3H, $\mathit{CH}_3(CH_2)_3P$), 1.05–1.75 (m, 6H, $CH_3(\mathit{CH}_2)_3P$), 1.80 (s, 3H, CH_3COO)

$\mathrm{Ru_4(CO)_8(CH_3COO)_4[P(OEt)_3]_2}$ [b]	2046(vs), 1996(sh), 1989(vs), 1980(vs), 1950(vw), 1924(s), 1900(vw)	1568(s), 1545(w), 1436(m), 1390(vw), 1348(vw)	1.12(t, 18H, $CH_3\mathrm{CH_2OP}$), 2.05(s, 12H, $CH_3\mathrm{COO}$), 4.02(m, 12H, $\mathrm{CH_3}CH_2\mathrm{OP}$)
$\mathrm{Ru_2(CO)_4(CH_3COO)_2[P(OEt)_3]_2}$ [b]	2038(vs), 1993(s), 1968(vs), 1940(vw), 1922(vw)	1582(s), 1480(vw), 1455(sh), 1437(s), 1391(w) 1348(w)	1.19(t, 18H, $CH_3\mathrm{CH_2OP}$), 1.77(s, 6H, $CH_3\mathrm{COO}$), 3.95–4.30 (m, 12H, $\mathrm{CH_3}CH_2\mathrm{OP}$)
$\mathrm{Ru_2(CO)_4(CH_3COO)_2(PCy_3)_2 \cdot C_6H_5CH_3}$ [a]	2013(vs), 1965(s), 1937(vs), 1908(vw), 1884(vw)	1579(s), 1460(sh), 1445(sh), 1435(s), 1342(w), 1324(w)	
$\mathrm{Ru_4(CO)_8(OOCCH_2CH_2COO)_2(PBu_3)_4}$ [b]	2018(vs), 2012(sh), 1972(m), 1965(sh), 1948(vs), 1938(sh), 1916(vw), 1895(vw)	1584(m), 1465(w), 1458(w), 1430(m),1405(w), 1380(w), 1322(vw), 1302(w)	0.94(t, 36H, $CH_3\mathrm{(CH_2)_3P}$), 1.20–2.10(m, 72H, $\mathrm{CH_3}(CH_2)_3\mathrm{P}$), 2.34(s, 8H, $\mathrm{OOC}CH_2CH_2\mathrm{COO}$)
$\mathrm{Ru_4(CO)_8(OOCCH_2CH_2CH_2CH_2COO)_2(PBu_3)_4}$ [b]	2016(vs), 2010(sh), 1971(s), 1965(sh), 1946(vs), 1936(sh), 1946(vs), 1936(sh), 1918(vw), 1896(vw)	1579(s), 1468(w), 1452(w), 1445(w), 1428(m), 1420(sh), 1379(w), 1316(w)	0.94(t, 36H, $CH_3\mathrm{(CH_2)_3P}$), 1.20–2.05(m, 80H, $\mathrm{CH_3}(CH_2)_3\mathrm{P}$, and $\mathrm{OOCCH_2}CH_2CH_2\mathrm{CH_2COO}$), 2.07–2.28(m, 8H, $\mathrm{OOC}CH_2\mathrm{CH_2CH_2}CH_2\mathrm{COO}$)

[a] KBr pellets. [b] C_6D_{12} as solvent.

Materials

$Ru_3(CO)_{12}$ [12], $[Ru_2(CO)_4(CH_3COO)_2]_n$ [3], $Ru_2(CO)_4(CH_3COO)_2(PBu_3)_2$ [3], $Ru_4(CO)_8(CH_3COO)_4(PBu_3)_2$ [2] were prepared by known procedures.

Acetic, oxalic, malonic, succinic and adipic acids, tri-n-butyl phosphine, triethylphosphite and tricyclohexylphosphine were commercial products. Solvents were purified by standard procedures and were oxygen free.

IR and NMR data are reported in Table 1. Elemental analyses and the results of molecular weight determinations are reported in Table 2.

Preparation of complexes

$Ru_2(CO)_4(CH_3COO)_2[P(OEt)_3]_2$ (IIb). A suspension of I (0.358 g, 1.66 mg-atoms Ru) in benzene (10 ml) containing $P(OEt)_3$ (0.297 g, 1.79 mmol) was refluxed under nitrogen to complete dissolution of the solid. The solution was then evaporated to dryness under vacuum and the residue crystallized from n-hexane (3 ml) at −20°C. After two crystallizations $Ru_2(CO)_4(CH_3COO)_2[P(OEt)_3]_2$ (0.420 g, 66.2% yield) was isolated as yellow-grey crystals.

$Ru_2(CO)_4(CH_3COO)_2(PCy_3)_2 \cdot C_6H_5CH_3$ (IIc). A suspension of I (0.305 g, 1.41 mg-atoms Ru) in toluene (10 ml) and PCy_3 (0.391 g, 1.40 mmol) was refluxed for 8 h

TABLE 2

ELEMENTAL ANALYSES AND MOLECULAR WEIGHT DETERMINATIONS OF SOME RUTHENIUM CARBONYL CARBOXYLATES

	Elemental analyses (Found (calcd.) (%))		Mol.wt.	
	C	H	(Found (calcd.))	Concentration [a] (g/l)
$[Ru_2(CO)_4(OOCCOO)]_n$	18.10	0.00	–	–
	(17.92)	(0.00)		
$[Ru_2(CO)_4(OOCCH_2COO)]_n$	20.49	0.50	–	–
	(20.20)	(0.48)		
$[Ru_2(CO)_4(OOCCH_2CH_2COO)]_n$	22.91	1.10	–	–
	(22.33)	(0.94)		
$[Ru_2(CO)_4(OOCCH_2CH_2CH_2CH_2COO)]_n$	26.50	1.90	–	–
	(26.21)	(1.76)		
$Ru(CO)_2(CH_3COO)_2(PBu_3)_2$	52.81	9.04	685	4.000
	(53.00)	(8.90)	(679.82)	
$Ru_2(CO)_5(CH_3COO)_2(PBu_3)$	38.42	5.13	n.d.	
	(38.07)	(5.02)	(662.61)	
$Ru_4(CO)_8(CH_3COO)_4[P(OEt)_3]_2$	27.93	3.56	1221	7.991
	(28.10)	(3.54)	(1196.87)	
$Ru_2(CO)_4(CH_3COO)_2[P(OEt)_3]_2$	31.20	4.67	769	3.784
	(31.42)	(4.75)	(764.60)	
$Ru_2(CO)_4(CH_3COO)_2(PCy_3)_2 \cdot C_6H_5CH_3$	56.69	7.42	1075	1.169
	(56.44)	(7.43)	(1085.29)	
$Ru_4(CO)_8(OOCCH_2CH_2COO)_2(PBu_3)_4$	46.18	6.99	1680	10.820
	(46.04)	(7.01)	(1669.81)	
$Ru_4(CO)_8(OOCCH_2CH_2CH_2CH_2COO)_2(PBu_3)_4$	48.04	7.33	1664	3.695
	(47.32)	(7.24)	(1725.92)	

[a] Toluene as solvent.

under nitrogen. The yellow material formed was separated from the cooled reaction mixture and crystallized from toluene, yielding IIc (0.612 g, 80% yield).

$Ru_4(CO)_8(CH_3COO)_4[P(OEt)_3]_2$ (IIIb). A mixture of I (0.392 g, 1.81 mg-atoms Ru), $P(OEt)_3$ (0.152 g, 0.91 mmol) in benzene (6 ml) was sealed under nitrogen, in a Pyrex tube, which was then placed in a rocking autoclave and heated at 100°C for 72 h. A yellow solution was then recovered together with unreacted I. The product recovered from a small portion of this solution by distillation of the solvent was dissolved in C_6D_6 for NMR analysis. The NMR spectrum showed two singlets at δ(TMS) 1.77 and 2.05, due to the acetyl groups of IIb and IIIb respectively, in the ratio 0.68/1. The solvent was evaporated under vacuum from the crude solution and the residue was dissolved in the minimum volume of boiling n-hexane; the solution was kept at −20°C to give crystals of IIIb (0.275 g, 50.8% yield).

$Ru(CO)_2(CH_3COO)_2(PBu_3)_2$ (IVa). (a) A suspension of I (0.292 g, 1.35 mg-atoms Ru) in benzene (5 ml) after addition of PBu_3 (0.59 g, 2.92 mmol) was heated under nitrogen, in a rocking stainless steel autoclave at 150°C for 88 h. The pale yellow solution formed was evaporated to dryness. The residue was crystallized from n-pentane (−78°C) to give IVa as white crystals (0.275 g, 30% yield).

(b) A suspension of I (0.485 g, 2.24 mg-atoms Ru) in acetic acid (5 ml) after addition of PBu_3 (0.92 g, 4.55 mmol) was refluxed for 8 h. The solution thus formed was worked up as described above to give IVa (0.99 g, 65% yield).

(c) A solution of $Ru_3(CO)_{12}$ (0.196 g, 0.92 mg-atoms Ru) and PBu_3 (0.726 g, 3.59 mmol) in 4-methylpentan-2-one (18 ml) was refluxed for 8 h under nitrogen to yield $Ru(CO)_3(PBu_3)_2$ [4]. Acetic acid (1.2 ml) was added, and the mixture was refluxed for 6 h. After work-up IVa was recovered in 73.5% yield.

$Ru_2(CO)_5(CH_3COO)_2(PBu_3)$ (Va). A solution of $Ru_4(CO)_8(CH_3COO)_4(PBu_3)_2$ (IIIa) (0.100 g, 0.079 mmol) in n-hexane (10 ml) was stirred under carbon monoxide at atmospheric pressure for 8 h. The pale yellow solution formed was kept at −78°C to give yellow crystals (0.084 g, 80% yield) of $Ru_2(CO)_5(CH_3COO)_2(PBu_3)$.

A solution of Va (0.100 g) in n-hexane (5 ml) was heated at 50°C for 5 h, then kept at −78°C to give yellow orange crystals, which had an IR spectrum identical to that of IVa.

$[Ru_2(CO)_4(OOCCOO)]_n$. $Ru_3(CO)_{12}$ (1.0 g, 4.69 mg-atoms Ru) and oxalic acid (1.0 g, 11.1 mmol) in toluene (15 ml) and dioxane (10 ml) were refluxed under nitrogen for 24 h. A deep red solution was rapidly formed from which a yellow-orange solid slowly separated. The formation of the solid was accelerated by flushing the apparatus with nitrogen to remove the evolved carbon monoxide. The solid was filtered off from the hot suspension and washed with ethyl alcohol and diethyl ether, then dried under vacuum (0.40 g, 42.3% yield).

$[Ru_2(CO)_4(OOCCH_2COO)]_n$. A mixture of $Ru_3(CO)_{12}$ (1.0 g, 4.69 mg-atoms Ru) and malonic acid (1.0 g, 9.61 mmol) in benzene (15 ml) and dioxane (10 ml) was refluxed under a slow flow of nitrogen for 24 h. A deep red solution was rapidly formed, from which a yellow solid separated. The solid separated from the hot suspension by filtration was washed with dioxane and diethyl ether and then dried under vacuum (0.90 g, 99.4% yield).

$[Ru_2(CO)_4(OOCCH_2CH_2COO)]_n$. A mixture of $Ru_3(CO)_{12}$ (1.0 g, 4.69 mg-atoms Ru) and succinic acid (1.0 g, 8.47 mmol) in toluene (50 ml)/dioxane (20 ml) was refluxed for 24 h under nitrogen. A deep red solution was rapidly formed, from which a yellow orange solid slowly separated. The formation of the solid was

accelerated by flushing the apparatus with nitrogen to remove the evolved carbon monoxide. The solid was separated from the hot suspension by filtration, washed with acetone and diethyl ether, then dried under vacuum (1.0 g, 99% yield).

$Ru_4(CO)_8(OOCCH_2CH_2COO)_2(PBu_3)_4$. PBu_3 (0.5 g, 2.47 mmol) was added to a suspension of $[Ru_2(CO)_4(OOCCH_2CH_2COO)]_n$ (0.5 g, 2.32 mg-atoms Ru) in benzene (25 ml) and the mixture was then refluxed for 24 h under nitrogen. The resulting yellow solution was evaporated to dryness under vacuum and the residue dissolved in hot n-heptane (15 ml). Yellow crystals of $Ru_4(CO)_8(OOCCH_2CH_2COO)_2(PBu_3)_4$ were obtained by cooling (0.684 g, 70% yield after three crystallizations).

$[Ru_2(CO)_4(OOCCH_2CH_2CH_2CH_2COO)]_n$. A mixture of $Ru_3(CO)_{12}$ (1.0 g, 4.69 mg-atoms Ru) and adipic acid (1.0 g, 6.85 mmol) in toluene (25 ml) was heated to reflux for 24 h. A deep red solution was rapidly formed from which a yellow orange solid slowly separated. The formation of the solid was accelerated by flushing the apparatus with nitrogen to remove the evolved carbon monoxide. The solid was separated from the hot solution, then washed with methanol and diethyl ether and dried under vacuum (1.0 g, 93% yield).

$Ru_4(CO)_8(OOCCH_2CH_2CH_2CH_2COO)_2(PBu_3)_4$. PBu_3 (0.46 g, 2.27 mmol) was added to a suspension of $[Ru_2(CO)_4(OOCCH_2CH_2CH_2CH_2COO)]_n$ (0.5 g, 2.18 mg-atoms Ru) in benzene (25 ml) and the mixture was refluxed for 24 h under nitrogen. The resulting yellow solution was evaporated to dryness under vacuum and the residue dissolved in hot n-heptane (5 ml). Yellow crystals of $Ru_4(CO)_8(OOCCH_2CH_2CH_2CH_2COO)_2(PBu_3)_4$ were obtained by cooling (0.6 g, 64% yield after two crystallizations).

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