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ASYMMETRIC SYNTHESIS BY CHIRAL RUTHENIUM COMPLEXES

XI *. ASYMMETRIC HYDROGENATION OF TIGLIC ACID IN THE PRESENCE OF PHOSPHINE SUBSTITUTED RUTHENIUM CARBONYL CARBOXYLATES

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Summary

The enantioface-discriminating hydrogenation of tiglic acid in the presence of (−)-DIOP substituted carbonyl carboxylato complexes of ruthenium has been investigated in order to identify the factors affecting the stereoselectivity of this reaction. The carboxylato ligand present in the catalytic intermediate does not seem to make a significant contribution to the stereoselectivity of this process. The stereoselectivity seems to be associated with the presence of the optically active phosphine. The catalytic system develops during the reaction through intermediates having a higher enantioface-discriminating activity than the initial and the final ruthenium complexes.

Introduction

Phosphine substituted ruthenium carbonyl carboxylates have been shown to be effective catalysts in the hydrogenation of carboxylic acids [2] and their esters [3]. We have studied the possibility of using this class of compounds, after introduction of a chiral phosphine, as catalysts in the enantioface-discriminating hydrogenation of a prochiral unsaturated substrate.

Ruthenium carbonyl carboxylates of the type $Ru_4(CO)_8[OOC(CH_2)_nCOO]_2[(-)\text{-DIOP}]_2$ (with $n = 0, 1, 2, 3$) were chosen as catalyst precursors. Tributylphosphine-substituted catalysts of this type have been previously used with success in the reduction of C=C and C=O double bonds [4].

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* For part X see ref. 1.

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Results and discussion

Tiglic acid was selected as substrate. The reaction conditions chosen, after preliminary tests, were 100°C, 130 atm of hydrogen and a 1/1 toluene/ethanol mixture as solvent.

All the catalysts used (Table 1), whatever the carboxylate ligand present, gave, under comparable conditions, (+)(*S*)-2-methylbutanoic acid of the same optical purity (~ 35%). This suggests either that the carboxylate group does not influence the steric course of the reaction or that during the reaction the catalytic intermediate is converted into the same catalytically active species in all the cases examined.

To gain information about the variation of the properties of the catalytic system during the reaction we have determined the value of the optical purity of the product formed at various conversion degrees. The results, reported in Table 2, show that the optical purity of the product increases gradually to reach a value of 42% under the conditions used. This behaviour might be interpreted in terms of a cooperative effect due to the incorporation of the optically active reaction product in the catalytic intermediate as a result of a displacement reaction. To check the validity of this hypothesis we examined the activity of the catalytic system recovered at the end of one of our standard experiments by using it again as catalyst in another hydrogenation of tiglic acid. This procedure was repeated twice with the same catalyst (Table 3). While the product obtained from the first re-use of the catalyst showed an optical purity higher than that obtained from the first reaction, in the subsequent experiment the optical purity of the product was lower, and just above that from the initial reaction.

In order to get more information on the role of the carboxylato group present in the catalytic precursor and, in particular, on the influence of its configuration on the steric course of this reaction we synthesized complexes of the type $\{Ru_2(CO)_4(\text{carboxylato})_2[(-)\text{-DIOP}]\}_m$, where the carboxylato residue is derived from either (*S*)-, (*R*)-, or (*R*)(*S*)-2-methylbutanoic acid. The optical purity of the product obtained by use of these complexes as catalyst precursors was not influenced by the configuration of the carboxylato ligand (Table 4). This may be due either to a real absence of influence of the configuration of the carboxylato ligand on the enantioface-discrimination ability of the catalyst or to a rapid exchange of this ligand with the acid present as substrate. In fact, when $\{Ru_2(CO)_4[(S)\text{-}(OOCCH(CH_3)C_2H_5)]_2[(-)\text{-DIOP}]\}_m$ was refluxed in toluene with tiglic acid, an

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TABLE 1

HYDROGENATION OF TIGLIC ACID TO (+)(*S*)-2-METHYLBUTANOIC ACID IN THE PRESENCE OF $Ru_4(CO)_8(\text{carboxylato})_2[(-)\text{-DIOP}]_2$.

Substrate 20 mmol; moles substrate/mg-atoms Ru 1000; $p(H_2)$ 130 atm; *T* 100°C; 1/1 toluene/ethanol 10 ml

Catalytic precursor [a]	Conv. (%)	Reaction time (h)	Optical purity (%)
$Ru_4(CO)_8(oxa)_2[(-)\text{-DIOP}]_2$	100	16	34.0
$Ru_4(CO)_8(mal)_2[(-)\text{-DIOP}]_2$	88.0	6	34.7
$Ru_4(CO)_8(suc)_2[(-)\text{-DIOP}]_2$	100	216	35.0
$Ru_4(CO)_8(glu)_2[(-)\text{-DIOP}]_2$	99.0	66	35.2

[a] oxa = OOCCOO; mal = $OOCCH_2COO$; suc = $OOCCH_2CH_2COO$; glu = $OOCCH_2CH_2CH_2COO$.

TABLE 2

HYDROGENATION OF TIGLIC ACID TO (+)(*S*)-2-METHYLBUTANOIC ACID IN THE PRESENCE OF $Ru_4(CO)_8(OOCCH_2COO)_2[(-)\text{-DIOP}]_2$: OPTICAL PURITY OF PRODUCT AT VARIOUS DEGREES OF CONVERSION

Substrate 20 mmol; moles substrate/mg-atoms Ru 1000; $p(H_2)$ 130 atm; *T* 80°C; 1/1 toluene/ethanol 10 ml.

Conversion (%)	Reaction time (h)	Optical purity (%)
15.5	5	32.8
53.0	20	35.8
99.0	65	41.8

TABLE 3

HYDROGENATION OF TIGLIC ACID TO (+)(*S*)-2-METHYLBUTANOIC ACID USING THE CATALYTIC SYSTEM PRESENT AT THE END OF THE PREVIOUS RUN

Toluene/ethanol (1/1) 60 ml; $p(H_2)$ 130 atm; *T* 100°C; catalytic precursor of run 1 $Ru_4(CO)_8(OOCCH_2COO)_2[(-)\text{-DIOP}]_2$ 0.12 mg-atoms Ru; moles substrate/mg-atoms Ru 1000

Run No.	Reaction time (h)	Enantiomeric discrimination (%)
1	8	35.2
2	10	51.2
3	13	37.8

TABLE 4

HYDROGENATION OF TIGLIC ACID TO (+)(*S*)-2-METHYLBUTANOIC ACID IN THE PRESENCE OF $\{Ru_2(CO)_4[OOCCH(CH_3)C_2H_5]_2[(-)\text{-DIOP}]\}_m$: INFLUENCE OF THE CONFIGURATION OF THE CARBOXYLATO LIGAND

Substrate 30 mmol; moles substrate/mg-atoms Ru 1310; $p(H_2)$ 130 atm; 1/1 toluene/ethanol 15 ml; *T* 80°C

Predominant configuration of the acid used to prepare the carboxylato derivative	Conversion (%)	Reaction time (h)	Optical purity (%)
(*R*)(*S*)	100	29	38.8
(*S*) 98.9%	84.7	25	40.3
(*R*) 81.9%	80.0	27	40.2

TABLE 5

HYDROGENATION OF TIGLIC ACID TO (+)(*S*)-2-METHYLBUTANOIC ACID IN THE PRESENCE OF $Ru_2(CO)_4[(S)\text{-}(OOCCH(CH_3)C_2H_5)]_2L_2$: INFLUENCE OF THE LIGAND

Substrate 30 mmol; moles substrate/mg-atoms Ru 1310; 1/1 toluene/ethanol 15 ml; $p(H_2)$ 130 atm, *T* 100°C

L_2	Conversion (%)	Reaction time (h)	Optical purity [a] (%)
$(PBu_3)_2$	90.0	80	0.0
$(PPh_3)_2$	73.7	153	1.9
(−)-DIOP	95.0	4	37.3

[a] Value obtained after correction for the presence of the (+)(*S*)-2-methylbutanoic acid present as ligand in the catalyst precursor.

TABLE 6

INFRARED SPECTRA, IN THE 2200–1200 cm^{-1} REGION, OF THE RUTHENIUM CARBOXYLATES

Compound	ν(CO) (cm^{-1})	Other bands (cm^{-1})
(+)-$Ru_4(CO)_8(OOCCOO)_2[(-)$-DIOP$]_2$ [a]	2062(w), 2030(s), 1988(m), 1958(vs), 1935(sh)	1625(m), 1485(vw), 1438(w), 1382(vw), 1320(m)
(+)-$Ru_4(CO)_8(OOCCOO)_2[(-)$-DIOP$]_2$ [b]	2038(vs), 1993(m), 1965(vs)	1621(m), 1589(m), 1485(vw), 1438(w), 1400(w), 1320(m)
(+)-$Ru_4(CO)_8(OOCCH_2COO)_2[(-)$-DIOP$]_2$ [a]	2030(sh), 2025(vs), 1986(m), 1955(vs), 1930(sh)	1620(vw), 1585(m), 1542(vw), 1485(vw), 1435(m), 1410 (vw), 1371(m)
(+)-$Ru_4(CO)_8(OOCCH_2COO)_2[(-)$-DIOP$]_2$ [b]	2030(vs), 1989(m), 1962(vs), 1936(w)	1590(s), 1575(sh), 1487(vw), 1439(m), 1375(m)
(+)-$Ru_4(CO)_8(OOCCH_2CH_2COO)_2[(-)$-DIOP$]_2$ [a]	2022(vs), 1984(m), 1952(vs), 1929(w)	1580(m), 1575(m), 1487(w), (1435(m), 1430(m), 1408(w), 1381(w), 1308(w)
(+)-$Ru_4(CO)_8(OOCCH_2CH_2COO)_2[(-)$-DIOP$]_2$ [b]	2024(vs), 1988(m), 1960(vs), 1935(sh)	1582(s), 1498(w), 1435(m), 1405(w), 1375(vw)
(+)-$Ru_4(CO)_8(OOCCH_2CH_2CH_2COO)_2[(-)$-DIOP$]_2$ [a]	2024(vs), 1982(s), 1949(vs), 1924(w), 1905(sh)	1575(s), 1540(sh), 1485(w), 1460(w), 1438(s), 1420(m), 1400(sh), 1381(w), 1348(w), 1312(w)
(+)-$Ru_4(CO)_8(OOCCH_2CH_2CH_2COO)_2[(-)$-DIOP$]_2$ [b]	2028(vs), 1988(m), 1964(vs), 1935(vw)	1582(s), 1488(vw), 1463(w), 1441(w), 1422(w), 1400(w), 1381(vw), 1340(w), 1312(vw)
$\{Ru_2(CO)_4[(S)\text{-}(OOCCH(CH_3)C_2H_5)]_2\}_n$ [a]	2100(w), 2051(vs), 1995(vs), 1989(vs), 1961(vs), 1937(d), 1918(sh)	1555(sh), 1542(s), 1466(m), 1455(sh), 1416(s), 1382(vw), 1371(vw), 1340(w), 1303(m)
$\{Ru_2(CO)_4[(S)\text{-}(OOCCH(CH_3)C_2H_5)]_2\cdot[(S)\text{-}(HOOCCH(CH_3)C_2H_5)]\}_n$ [a]	2100(w), 2040(vs), 1995(sh), 1987(s), 1959(vs), 1928(sh), 1920(sh)	1670(m), 1561(s), 1553(sh), 1466(w), 1417(m), 1382(vw), 1370(vw), 1336(vw), 1316(w)
$\{Ru_2(CO)_4[(S)\text{-}(OOCCH(CH_3)C_2H_5)]_2\cdot[(S)\text{-}(HOOCCH(CH_3)C_2H_5)]\}_n$ [b]	2055(sh), 2050(sh), 2044(vs), 1995(m), 1969(vs), 1938(vw)	1712(vw), 1680(m), 1563(m), 1465(w), 1416(w)
(−)-$Ru_2(CO)_4[(S)\text{-}(OOCCH(CH_3)C_2H_5)]_2(PBu_3)_2$ [a]	2014(vs), 1964(s), 1937(vs), 1912(sh), 1888(vw)	1572(s), 1465(m), 1454(sh), 1421(m), 1377(vw), 1365(vw), 1312(w)
(−)-$Ru_2(CO)_4[(S)\text{-}(OOCCH(CH_3)C_2H_5)]_2(PBu_3)_2$ [b]	2018(vs), 2011(sh), 1972(m), 1947(vs), 1940(sh), 1917(vw), 1896(vw)	1574(m), 1466(w), 1460(sh), 1421(w), 1380(vw), 1367(vw), 1342(vw), 1312(w)
(+)-$Ru_2(CO)_4[(S)\text{-}(OOCCH(CH_3)C_2H_5)]_2(PPh_3)_2$ [a]	2020(vs), 1978(s), 1944(vs), 1917(w), 1905(vw), 1894(vw)	1586(sh), 1564(s), 1481(w), 1466(w), 1438(sh), 1433(m), 1422(m), 1382(vw), 1369(vw), 1333(vw), 1311(w)
(+)-$Ru_2(CO)_4[(S)\text{-}(OOCCH(CH_3)C_2H_5)]_2(PPh_3)_2$ [b]	2027(vs), 1985(m), 1959(vs), 1931(w)	1577(sh), 1568(m), 1484(vw), 1466(vw), 1435(w), 1423(w), 1313(vw)

$(+)\text{-}\{Ru_2(CO)_4[(S)\text{-}(OOCCH(CH_3)C_2H_5)]_2[(-)\text{-}DIOP]\}_m$ [a]	2021(vs), 1978(m), 1948(vs), 1919(sh)	1590(sh), 1565(m), 1535(sh), 1484(vw), 1465(w), 1460(sh), 1434(w), 1421(m), 1381(w), 1375(sh), 1315(w)
$(+)\text{-}\{Ru_2(CO)_4[(S)\text{-}(OOCCH(CH_3)C_2H_5)]_2[(-)\text{-}DIOP]\}_m$ [b]	2025(vs), 1981(m), 1955(vs), 1923(vw)	1590(sh), 1568(m), 1487(vw), 1466(w), 1460(sh), 1434(w), 1421(w), 1380(vw), 1313(vw)
$\{Ru_2(CO)_4(OOCCH(CH_3)C_2H_5)_2\}_n$ [a]	2100(w), 2042(vs), 1999(vs), 1992(sh), 1974(vs), 1940(sh), 1922(sh)	1548(vs), 1538(sh), 1466(m), 1455(sh), 1438(vw), 1413(s), 1382(vw), 1371(vw), 1340(vw), 1315(sh), 1300(m)
$(+)\text{-}\{Ru_2(CO)_4(OOCCH(CH_3)C_2H_5)_2[(-)\text{-}DIOP]\}_m$ [a]	2021(vs), 1978(m), 1948(vs), 1919(sh)	1590(sh), 1565(s), 1535(sh), 1484(w), 1465(w), 1460(sh), 1434(w), 1421(m), 1381(w), 1375(sh), 1315(w)
$(+)\text{-}\{Ru_2(CO)_4(OOCCH(CH_3)C_2H_5)_2[(-)\text{-}DIOP]\}_m$ [b]	2025(vs), 1981(m), 1955(vs), 1923(vw)	1590(sh), 1568(m), 1487(vw), 1466(w), 1460(sh), 1434(w), 1421(w), 1380(vw), 1313(vw)
$\{Ru_2(CO)_4[(R)\text{-}(OOCCH(CH_3)C_2H_5)]_2\}_n$ [a]	2100(w), 2050(vs), 1995(vs), 1989(vs), 1961(vs), 1937(s), 1916(sh)	1560(sh), 1542(vs), 1534(sh), 1465(m), 1455(sh), 1414(s), 1383(vw), 1370(vw), 1340(w), 1303(m)
$(+)\text{-}\{Ru_2(CO)_4[(R)\text{-}(OOCCH(CH_3)C_2H_5)]_2[(-)\text{-}DIOP]\}_m$ [a]	2021(vs), 1978(m), 1948(vs), 1919(sh)	1590(sh), 1565(s), 1535(sh), 1484(vw), 1465(w), 1460(sh), 1434(w), 1421(m), 1381(w), 1375(sh), 1315(w)
$(+)\text{-}\{Ru_2(CO)_4[(R)\text{-}(OOCCH(CH_3)C_2H_5)]_2[(-)\text{-}DIOP]\}_m$ [b]	2025(vs), 1981(m), 1955(vs), 1923(vw)	1590(sh), 1568(m), 1487(vw), 1466(w), 1460(sh), 1434(w), 1421(w), 1380(vw), 1313(vw)
$\{Ru_2(CO)_4(OOCC(CH_3){=}CHCH_3)_2\}_n$ [a]	2098(w), 2043(vs), 2001(vs), 1990(sh), 1979(vs), 1963(sh), 1940(sh)	1656(m), 1625(vw), 1540(s), 1513(vs), 1466(vs), 1441(vw), 1416(vs), 1386(sh), 1378(m), 1328(w), 1310(w)
$(+)\text{-}\{Ru_2(CO)_4(OOCC(CH_3){=}CHCH_3)_2[(-)\text{-}DIOP]\}_m$ [a]	2022(vs), 1980(m), 1950(vs), 1920(w)	1657(w), 1590(vw), 1548(m), 1485(vw), 1460(vw), 1435(m), 1412(m), 1382(w), 1378(sh), 1328(w)
$(+)\text{-}\{Ru_2(CO)_4(OOCC(CH_3){=}CHCH_3)_2[(-)\text{-}DIOP]\}_m$ [c]	2023(vs), 1979(m), 1951(vs), 1918(w)	1718(vw), 1658(vw), 1587(vw), 1548(m), 1486(w), 1440(sh), 1434(m), 1413(m), 1380(w), 1373(w)

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[a] KBr pellet. [b] C_6D_{12} solution. [c] C_6D_6 solution.

exchange took place with release of 2-methylbutanoic acid.

All the results described above seem to indicate that the stereoselectivity of this type of catalyst resides mainly in the chiral phosphine ligand. Such an indication was confirmed by the results obtained from the hydrogenation of tiglic acid in the presence of catalyst precursors of the type $Ru_2(CO)_4[(S)\text{-}(OOCCH(CH_3)C_2H_5)]_2L_2$, where an asymmetric carboxylato ligand was accompanied by (−)-DIOP, PBu_3 or PPh_3 (Table 5). The product had an optical purity of zero when the phosphine was PBu_3, and 1.6% when the phosphine was PPh_3. The residual low optical activity in the latter case may be attributed to a fairly low rate for exchange of the carboxylato substituent of the catalyst with tiglic acid present as substrate, and may therefore be taken as an indication of a certain influence of the chiral carboxylato ligand in the catalytic intermediate on the stereoselectivity of the catalyst when very rapid exchange is avoided.

In order to minimize the exchange between the optically active carboxylato ligand of the catalyst $\{Ru_2(CO)_4[(S)\text{-}(OOCCH(CH_3)C_2H_5)]_2[(-)\text{-DIOP}]\}_m$ and tiglic acid we performed hydrogenation experiments of tiglic acid with this catalyst in the presence of substantial amounts of (+)(*S*)-2-methylbutanoic acid while keeping the concentration of the substrate low. This was achieved by adding a fair amount of (+)(*S*)-2-methylbutanoic acid to the initial reaction mixture and then adding tiglic acid subsequently in small portions. Even under these conditions the optical purity of the reaction product was not improved; it was only 28.6%, compared with 34.7% under normal conditions.

The initial increase followed by a considerable decrease of the optical purity of the product as the catalyst is aged (Table 3) can probably be ascribed to a change in the catalytic system which slowly forms an intermediate having a fair stereoselective activity. This intermediate is in turn transformed into other complexes having lower activity. Racemization of the product under conditions, which might be an alternative cause of the low optical purity, was found in fact to be extremely low (1.6% after 40 h).

Finally we hydrogenated the (−)-DIOP substituted ruthenium carbonyl carboxylato derivative of tiglic acid in order to see if the acid bound in the complex as carboxylato ligand was the one giving rise to the optically active hydrogenation product. The results obtained (9.2% optical purity) tend to exclude this hypothesis, and point towards a complexation of the substrate with the catalyst as a simple olefin. The formation of carboxylato complexes in our reaction system probably corresponds with a progressive change in the system in the direction of more stable species.

Experimental

Physical spectra were recorded on the following instruments: NMR, Perkin–Elmer R32 spectrometer; IR, Perkin–Elmer 580B Data System. GLC analyses were performed with a Perkin–Elmer Sigma 1 System. Molecular weight determinations based on the isopiestic method were performed using a Wescam model 233 instrument. Optical rotations were measured with Perkin–Elmer 241 polarimeter. Elemental analyses were performed with a Perkin–Elmer 240C elemental analyzer. IR and NMR data are reported in Tables 6 and 7, respectively. Elemental analyses, the results of molecular weight determinations and the sign and the values of the rotations are listed in Table 8.

Materials

Tiglic acid (Fluka), $(R)(S)$-2-methylbutanoic acid (Fluka), $(-)(S)$-2-methylbutanol (Fluka) b.p. 128°C, n_D^{25} 1.4086, $[\alpha]_D^{25}$ -5.820, optical purity 100%. $(+)(S)$-2-Methylbutanoic acid, prepared as described by Freudenberg et al. [5], had b.p. 110–111°C/72 mmHg, n_D^{25} 1.4041, $[\alpha]_D^{25}$ $+19.596$; the optical purity of the acid was 98.9% assuming $[\alpha]_{D\max}^{25}$ $+19.8$ [5], d_4^{25} 0.9313 for $(+)(S)$-2-methylbutanoic acid [6]. $(-)(R)$-2-Methylbutanoic acid, prepared by resolution of a racemic mixture as reported by Odham [7], had b.p. 110–112°C/75 mmHg, n_D^{25} 1.4042, $[\alpha]_D^{25}$ -16.28; the optical purity of the acid was 81.9% assuming $[\alpha]_{D\max}^{25}$ -19.8 [5], d_4^{25} 0.9313 for $(-)(R)$-2-methylbutanoic acid [6]. Tributylphosphine (Merck) and triphenylphosphine (Fluka) were commercial samples. $(-)$-DIOP, prepared by a known procedure [8], had m.p. 88–89°C, $[\alpha]_D^{20}$ -12.710 (c 0.70 in benzene).

Catalysts

$[Ru_2(CO)_4(OOCCOO)]_n$, $[Ru_2(CO)_4(OOCCH_2COO)]_n$, $[Ru_2(CO)_4(OOCCH_2CH_2COO)]_n$, $[Ru_2(CO)_4(OOCCH_2CH_2CH_2COO)]_n$ were prepared by a known procedure [9].

$Ru_4(CO)_8(OOCCOO)_2[(-)\text{-DIOP}]_2$. A suspension of $[Ru_2(CO)_4(OOCCOO)]_n$ (500 mg, 2.40 mg-atoms Ru) in benzene (25 ml) containing $(-)$-DIOP (620 mg, 1.24 mmol) was heated at 50°C under nitrogen until the solid completely dissolved. The solution was evaporated to dryness and the residue dissolved in dichloromethane. The addition of methanol gave yellow crystals of $Ru_4(CO)_8(OOCCOO)_2[(-)\text{-DIOP}]_2$ (180 mg, 0.10 mmol).

$Ru_4(CO)_8(OOCCH_2COO)_2[(-)\text{-DIOP}]_2$. $(-)$-DIOP (600 mg, 1.20 mmol) was added to a suspension of $[Ru_4(CO)_8(OOCCH_2COO)]_n$ (500 mg, 2.40 mg-atoms Ru) in benzene (25 ml) and the mixture was heated at 50°C for 2 h under nitrogen. The resulting yellow solution was evaporated to dryness under vacuum, and the residue was washed with ethanol and n-pentane. Yellow crystals of $Ru_4(CO)_8(OOCCH_2COO)_2[(-)\text{-DIOP}]_2$ (300 mg, 0.16 mmol) were obtained.

$Ru_4(CO)_8(OOCCH_2CH_2COO)_2[(-)\text{-DIOP}]_2$. A suspension of $[Ru_2(CO)_4(OOCCH_2CH_2COO)]_n$ (500 mg, 2.32 mg-atoms Ru) in benzene (25 ml) containing $(-)$-DIOP (580 mg, 1.16 mmol) was refluxed under nitrogen until the solid had completely dissolved. The solution was evaporated to dryness and the residue was dissolved in dichloromethane. Addition of methanol gave yellow crystals of $Ru_4(CO)_8(OOCCH_2CH_2COO)_2[(-)\text{-DIOP}]_2$ (350 mg, 1.9 mmol).

$Ru_4(CO)_8(OOCCH_2CH_2CH_2COO)_2[(-)\text{-DIOP}]_2$. $(-)$-DIOP (560 mg, 1.12 mmol) was added to a suspension of $[Ru_2(CO)_4(OOCCH_2CH_2CH_2COO)]_n$ (500 mg, 2.25 mg-atoms Ru) in benzene (25 ml) and the mixture was heated at 50°C for 24 h. The resulting yellow solution was evaporated to dryness under vacuum and the residue was dissolved in dichloromethane. Addition of methanol gave yellow needles of $Ru_4(CO)_8(OOCCH_2CH_2CH_2COO)_2[(-)\text{-DIOP}]_2$ (400 mg, 0.21 mmol).

$\{Ru_2(CO)_4[(S)\text{-}(OOCCH(CH_3)C_2H_5)]_2\}_n$. A mixture of triruthenium dodecacarbonyl (1.00 g, 4.69 mg-atoms Ru) and $(+)(S)$-2-methylbutanoic acid (600 mg, 5.87 mmol, optical purity 98.9%), in octane (15 ml) was refluxed for 45 h. A deep red solution was rapidly formed, and from this 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. $\{Ru_2(CO)_4[(S)\text{-}(OOCCH(CH_3)C_2H_5)]_2\}_n$ (1.0 g, 3.87 mg-atoms Ru) was separated from the hot suspension by centrifugation,

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TABLE 7

NMR SPECTRA OF THE RUTHENIUM CARBONYL CARBOXYLATES (Solvent CD_2Cl_2, TMS internal standard, δ(ppm))

$(+)\text{-}Ru_4(CO)_8(OOCCOO)_2[(-)\text{-DIOP}]_2$	1.28 (s, 3H, CH_3C), 1.67 (s, 3H, CH_3C), 2.48–2.98 (m, 2H, CH_2P), 2.98–3.50 (m, 2H, CH_2P), 3.72–4.04 (m, 1H, CHO), 4.28–4.60 (m, 1H, CHO), 6.96–7.28 (m, 4H, C_6H_5), 7.38–7.78 (m, 12H, C_6H_5), 7.78–8.18 (m, 4H, C_6H_5)
$(+)\text{-}Ru_4(CO)_8(OOCCH_2COO)_2[(-)\text{-DIOP}]_2$	0.99 (s, 6H, $(CH_3)_2C$), 2.64 (m, 4H, CH_2P), 3.45 (s, 2H, CH_2 $(COO)_2$), 4.15 (m, 2H, CH_2CH), 7.28–7.75 (m, 20H, C_6H_5)
$(+)\text{-}Ru_4(CO)_8(OOCCH_2CH_2COO)_2[(-)\text{-DIOP}]_2$	1.00 (s, 6H, $(CH_3)_2C$), 2.64 (m, 4H, CH_2P), 2.80 (s, 4H, CH_2COO), 3.87 (m, 2H, CH_2CH), 7.30–8.05 (m, 20H, C_6H_5)
$(+)\text{-}Ru_4(CO)_8(OOCCH_2CH_2CH_2COO)_2[(-)\text{-DIOP}]_2$	0.95 (s, 6H, $(CH_3)_2C$), 1.80–3.00 (m, 10H, CH_2P and $OOCCH_2CH_2CH_2COO$), 3.55 (m, 2H, $CH_2\mathit{CH}$), 7.22–7.95 (m, 20H, C_6H_5)
$\{Ru_2(CO)_4[(S)\text{-}(OOCCH(CH_3)C_2H_5)]_2\cdot$ $[(S)\text{-}HOOCCH(CH_3)C_2H_5)]\}_n$	0.75–1.28 (m, 12H, CH_3), 1.30–1.82 (m, 4H, CH_2), 2.28–2.74 (m, 2H, CH)
$(-)\text{-}Ru_2(CO)_4[(S)\text{-}(OOCCH(CH_3)C_2H_5)]_2(PBu_3)_2$	0.66–1.02 (m, 15H, CH_3), 1.10–2.05 (m, 20H, CH_2), 2.05–2.36 (m, 1H, CH)
$(+)\text{-}Ru_2(CO)_4[(S)\text{-}(OOCCH(CH_3)C_2H_5)]_2(PPh_3)_2$	0.51–0.79 (m, 6H, CH_3), 0.96–1.27 (m, 2H, CH_2), 1.86–2.18 (m, 1H, CH), 7.30–7.71 (m, 15H, C_6H_5)
$(+)\text{-}\{Ru_2(CO)_4[(S)\text{-}(OOCCH(CH_3)C_2H_5)]_2[(-)\text{-DIOP}]\}_m$	0.48–0.77 (m, 12H, $\mathit{CH_3}CH_2CH(\mathit{CH_3})COO$), 0.95 (s, 6H, $(CH_3)_2C$), 0.95–1.33 (m, 4H, $CH_3CH_2\mathit{CH}$), 1.68–1.98 (m, 2H, $CH_3\mathit{CH_2}CH$), 2.35–.2.65 (m, 4H, CH_2P), 3.63–3.95 (m, 2H, $CH_2\mathit{CHO}$), 7.20–7.80 (m, 20H, C_6H_5)
$(+)\text{-}\{Ru_2(CO)_4(OOCCH(CH_3)C_2H_5)_2[(-)\text{-DIOP}]\}_m$	0.48–0.83 (m, 12H, $\mathit{CH_3}CH_2CH(\mathit{CH_3})COO$), 0.94 (s, 6H, $(CH_3)_2C$), 0.94–1.30 (m, 4H, $CH_3CH_2\mathit{CH}$), 1.70–2.00 (m, 2H, $CH_3\mathit{CH_2}CH$), 2.35–2.68 (m, 4H, CH_2P), 3.64–3.88 (m, 2H, $CH_2\mathit{CHO}$), 7.12–7.70 (m, 20H, C_6H_5)
$(+)\text{-}\{Ru_2(CO)_4[(R)\text{-}(OOCCH(CH_3)C_2H_5)]_2[(-)\text{-DIOP}]\}_m$	0.47–0.80 (m, 12H, $\mathit{CH_3}CH_2CH(\mathit{CH_3})COO$), 0.92 (s, 6H, $(CH_3)_2C$), 0.95–1.30 (m, 4H, $CH_3CH_2\mathit{CH}$), 1.70–2.00 (m, 2H, $CH_3\mathit{CH_2}CH$), 2.38–2.70 (m, 4H, CH_2P), 3.58–3.90 (m, 2H, $CH_2\mathit{CHO}$), 7.22–7.75 (m, 20H, C_6H_5)
$(+)\text{-}\{Ru_2(CO)_4(OOCC(CH_3){=}CHCH_3)_2[(-)\text{-DIOP}]\}_m$	0.93 (s, 6H, $(CH_3)_2C$), 1.18–1.60 (m, 12H, $\mathit{CH_3}CH{=}C(\mathit{CH_3})COO$), 2.34–2.68 (m, 4H, CH_2P), 3.55–3.90 (m, 2H, $CH_2\mathit{CHO}$), 5.51–5.84 (m, 2H, $CH_3\mathit{CH}{=}C$), 7.12–7.75 (m, 20H, C_6H_5)

TABLE 8

ELEMENTAL ANALYSES, MOLECULAR WEIGHT AND ROTATIONS OF THE RUTHENIUM CARBONYL CARBOXYLATES

Compound	Elemental analyses (Found (calcd.) (%))		Molecular weight Found (Calcd.)	$[\alpha]_D^{25}$ [a]
	C	H		
$(+)\text{-Ru}_4(\text{CO})_8(\text{OOCCOO})_2[(-)\text{-DIOP}]_2$	49.12 (49.34)	3.62 (3.58)	1902 (1801.5)	+524.151
$(+)\text{-Ru}_4(\text{CO})_8(\text{OOCCH}_2\text{COO})_2[(-)\text{-DIOP}]_2$	49.98 (49.89)	3.77 (3.75)	1746 (1829.6)	+ 40.784 [b]
$(+)\text{-Ru}_4(\text{CO})_8(\text{OOCCH}_2\text{CH}_2\text{COO})_2[(-)\text{-DIOP}]_2$	50.11 (50.43)	3.95 (3.91)	1868 (1857.6)	+399.200
$(+)\text{-Ru}_4(\text{CO})_8(\text{OOCCH}_2\text{CH}_2\text{CH}_2\text{COO})_2[(-)\text{-DIOP}]_2$	50.43 (50.96)	4.05 (4.06)	1956 (1885.7)	+401.509
$\{\text{Ru}_2(\text{CO})_4[(S)\text{-(OOCCH(CH}_3)\text{C}_2\text{H}_5]_2\}_n$	32.29 (32.56)	3.43 (3.51)	– –	–
$\{\text{Ru}_2(\text{CO})_4[(S)\text{-(OOCCH(CH}_3)\text{C}_2\text{H}_5)]_2\cdot[(S)\text{-(HOOCCH(CH}_3)\text{C}_2\text{H}_5)]\}_n$	37.27 (36.89)	4.57 (4.56)	– –	– –
$(-)\text{-Ru}_2(\text{CO})_4[(S)\text{-(OOCCH(CH}_3)\text{C}_2\text{H}_5)]_2(\text{PBu}_3)_2$	49.75 (49.55)	8.06 (7.88)	853 (921.1)	− 8.301
$(+)\text{-Ru}_2(\text{CO})_4[(S)\text{-(OOCCH(CH}_3)\text{C}_2\text{H}_5)]_2(\text{PPh}_3)_2$	58.39 (57.69)	4.68 (4.65)	990 (1041.0)	+ 4.528 [c]
$(+)\text{-}\{\text{Ru}_2(\text{CO})_4[(S)\text{-(OOCCH(CH}_3)\text{C}_2\text{H}_5)]_2[(-)\text{-DIOP}]\}_m$	53.41 (53.25)	4.84 (4.97)	4255–9051 1015.0	+ 2.830
$\{\text{Ru}_2(\text{CO})_4[\text{OOCCH(CH}_3)\text{C}_2\text{H}_5]_2\}_n$	32.34 (32.56)	3.50 (3.51)	– –	–
$(+)\text{-}\{\text{Ru}_2(\text{CO})_4[\text{OOCCH(CH}_3)\text{C}_2\text{H}_5]_2[(-)\text{-DIOP}]\}_m$	53.48 (53.25)	5.15 (4.97)	3816–4632 (1015.0)	+ 24.530
$\{\text{Ru}_2(\text{CO})_4[(R)\text{-(OOCCH(CH}_3)\text{C}_2\text{H}_5)]_2\}_n$	31.97 (32.56)	3.48 (3.51)	– –	–
$(+)\text{-}\{\text{Ru}_2(\text{CO})_4[(R)\text{-(OOCCH(CH}_3)\text{C}_2\text{H}_5)]_2[(-)\text{-DIOP}]\}_m$	52.91 (53.25)	5.16 (4.97)	2896–4010 (1015.0)	+ 24.340
$\{\text{Ru}_2(\text{CO})_4[\text{OOCC(CH}_3)\text{=CHCH}_3]_2\}_n$	32.79 (32.82)	2.71 (2.75)	–	–
$(+)\text{-}\{\text{Ru}_2(\text{CO})_4[\text{OOCC(CH}_3)\text{=CHCH}_3]_2[(-)\text{-DIOP}]\}_m$	53.71 (53.46)	4.79 (4.59)	4713–11922 (1010.9)	+ 94.906

[a] *c* 0.53 g/100 ml toluene. [b] *c* 0.51. [c] Dichloromethane as solvent.

washed with n-pentane, and then dried under vacuum. The hot solution was cooled to give deep red crystals of $\{Ru_2(CO)_4[(S)\text{-}(OOCCH(CH_3)C_2H_5)]_2 \cdot [(S)\text{-}HOOCCH(CH_3)C_2H_5]\}_n$. When this compound was heated in n-octane it was transformed into $[Ru_2(CO)_4[(S)\text{-}(OOCCH(CH_3)C_2H_5]_2\}_n$ (140 mg, 0.54 mg-atoms Ru).

$Ru_2(CO)_4[(S)\text{-}(OOCCH(CH_3)C_2H_5)]_2(PBu_3)_2$. Tributylphosphine (470 mg, 2.32 mmol) was added to a suspension of $\{Ru_2(CO)_4[(S)\text{-}(OOCCH(CH_3)C_2H_5)]_2\}_n$ (2.32 mg-atoms Ru) in pentane (20 ml) and the mixture was stirred under nitrogen until the solid completely dissolved. The yellow orange solution was evaporated to dryness under vacuum and the residue dissolved in dichloromethane. Addition of methanol gave yellow crystals of $Ru_2(CO)_4[(S)\text{-}(OOCCH(CH_3)C_2H_5)]_2(PBu_3)_2$ (780 mg, 1.70 mg-atoms Ru), m.p. 59–60°C.

$Ru_2(CO)_4[(S)\text{-}(OOCCH(CH_3)C_2H_5)]_2(PPh_3)_2$. Triphenylphosphine (396 mg, 1.51 mmol) was added to a suspension of $\{Ru_2(CO)_4[(S)\text{-}(OOCCH(CH_3)C_2H_5)]_2\}_n$ (400 mg, 1.55 mg-atoms Ru) in toluene (15 ml) and the mixture was heated at 35°C under nitrogen until the solid completely dissolved. The yellow orange solution was evaporated to dryness. The residue was recrystallized from toluene containing a few drops of dichloromethane to give yellow crystals of $Ru_2(CO)_4[(S)\text{-}(OOCCH(CH_3)C_2H_5)]_2(PPh_3)_2$ (500 mg, 0.96 mg-atoms Ru), m.p. 234.5–235.5°C.

$\{Ru_2(CO)_4[(S)\text{-}(OOCCH(CH_3)C_2H_5)]_2[(-)\text{-}DIOP)\}_m$. A suspension of $\{Ru_2(CO)_4[(S)\text{-}(OOCCH(CH_3)C_2H_5)]_2\}_n$ (1.55 mg-atoms Ru) in toluene (35 ml) containing (−)-DIOP (386 mg, 0.77 mmol) was stirred under nitrogen until the solid had completely dissolved. The yellow solution was then evaporated to dryness under vacuum and the residue dissolved in dichloromethane. Addition of n-hexane gave yellow microcrystals of $\{Ru_2(CO)_4[(S)\text{-}(OOCCH(CH_3)C_2H_5)]_2[(-)\text{-}DIOP]\}_m$ (594 mg, 1.17 mg-atoms Ru).

$[Ru_2(CO)_4(OOCCH(CH_3)C_2H_5)_2]_n$. A suspension of triruthenium dodecacarbonyl (1.5 g, 7.04 mg-atoms Ru) and (*R*)(*S*)-2-methylbutanoic acid (720 mg, 7.05 mmol) in octane (30 ml) was refluxed for 24 h under nitrogen. A deep red solution was rapidly formed, and from this 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, washed with n-pentane and dried under vacuum to give $[Ru_2(CO)_4(OOCCH(CH_3)C_2H_5)_2]_n$ (1.65 g, 6.39 mg-atoms Ru).

$\{Ru_2(CO)_4(OOCCH(CH_3)C_2H_5)_2[(-)\text{-}DIOP]\}_m$. (−)-DIOP (193 mg, 0.39 mmol) was added to a suspension of $[Ru_2(CO)_4(OOCCH(CH_3)C_2H_5)_2]_n$ (200 mg, 0.78 mg-atoms Ru) in toluene (20 ml) and the mixture was stirred under nitrogen to complete the dissolution of the solid. The yellow solution was evaporated to dryness to give yellow microcrystals of $\{Ru_2(CO)_4(OOCCH(CH_3)C_2H_5)_2[(-)\text{-}DIOP]\}_m$ (390 mg, 0.77 mg-atoms Ru).

$\{Ru_2(CO)_4[(R)\text{-}(OOCCH(CH_3)C_2H_5)]_2\}_n$. A suspension of triruthenium dodecacarbonyl (1.14 g, 5.35 mg-atoms Ru) in octane (40 ml) containing (−)(*R*)-2-methylbutanoic acid (500 mg, 4.90 mmol, optical purity 81.9%) was refluxed for 24 h under nitrogen. A deep red solution was rapidly formed, and from this 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, washed with n-pentane, and dried under vacuum, to give $\{Ru_2(CO)_4[(R)\text{-}(OOCCH(CH_3)C_2H_5)]_2\}_n$ (1.265 g, 4.90 mg-atoms Ru).

$\{Ru_2(CO)_4[(R)\text{-}(OOCCH(CH_3)C_2H_5)]_2[(-)\text{-}DIOP]\}_m$. (−)-DIOP (193 mg, 0.39 mmol) was added to a suspension of $\{Ru_2(CO)_4[(R)\text{-}(OOCCH(CH_3)C_2H_5)]_2\}_n$ (200 mg, 0.78 mg-atoms Ru) in toluene (20 ml) and stirred under nitrogen to complete the dissolution of the solid. The yellow solution was evaporated to dryness to give yellow microcrystals of $\{Ru_2(CO)_4[(R)\text{-}(OOCCH(CH_3)C_2H_5)]_2[(-)\text{-}DIOP]\}_m$ (393 mg, 0.78 mg-atoms Ru).

$\{Ru_2(CO)_4[OOCC(CH_3)=CHCH_3]_2\}_n$. A suspension of triruthenium dodecacarbonyl (1.00 g, 4.69 mg-atoms Ru) in octane (20 ml) containing tiglic acid (500 mg, 4.99 mmol) was refluxed for 24 h under nitrogen. A deep red solution was rapidly formed, and from this a yellow orange solid slowly separated. The formation of the solid was accelerated by flushing the apparatus with nitrogen to remove the carbon monoxide evolved. The solid was filtered off, washed with n-pentane, and dried under vacuum to give $\{Ru_2(CO)_4[OOCC(CH_3)=CHCH_3]_2\}_n$ (883 mg, 3.44 mg-atoms Ru).

$\{Ru_2(CO)_4[OOCC(CH_3)=CHCH_3]_2[(-)\text{-}DIOP]\}_m$. A suspension of $\{Ru_2(CO)_4[OOCC(CH_3)=CHCH_3]_2\}_n$ (610 mg, 2.38 mg-atoms Ru) in toluene (25 ml) containing (−)-DIOP (570 mg, 1.14 mmol) was stirred, under nitrogen to complete the dissolution of the solid. The solution was evaporated to dryness and the residue was dissolved in dichloromethane. Addition of n-hexane gave yellow microcrystals of $\{Ru_2(CO)_4[OOCC(CH_3)=CHCH_3]_2[(-)\text{-}DIOP]\}_m$ (1.00 g, 1.98 mg-atoms Ru).

Hydrogenation procedure

The catalytic precursor and the appropriate amount of tiglic acid were placed in a 150 ml stainless steel rocking autoclave. Hydrogen was added up to the required pressure. The reaction was carried out by heating the autoclave at the desired temperature.

We describe, as an example, the procedure for the second experiment in Table 1.

Tiglic acid (2 g), $Ru_4(CO)_8(OOCCH_2COO)_2[(-)\text{-}DIOP]_2$ (9.1 mg), toluene (5 ml) and anhydrous ethanol (5 ml) were placed in the autoclave and hydrogen was admitted up to 130 atm at 20°C. The vessel was heated at 100°C for 6 h. GLC analysis of the product mixture using FFAP columns at 140°C, showed the presence of only 2-methylbutanoic acid and tiglic acid; from a calibration curve the conversion degree of tiglic acid was found to be 88%.

The product mixture was then treated with a saturated aqueous solution of sodium carbonate to neutrality. After extraction of the mixture with diethyl ether, the organic acid was recovered from the aqueous layer by acidification with sulfuric acid and extraction with diethyl ether. This gave 2-methylbutanoic acid of b.p. 103–105°C/91 mmHg, $\alpha^{25}_{D(l=1)}$ +6.166° and $[\alpha]^{25}_{D}$ +6.621. Its optical purity was 34.7%, based on $[\alpha]^{25}_{D(max)}$ 19.8 [5] and d^{25}_{4} 0.9313 [6].

Hydrogenation of tiglic acid with re-use of the catalyst (Table 3)

Tiglic acid (12.0 g) was hydrogenated in the presence of 56.1 mg $Ru_4(CO)_8(OOCCH_2COO)_2[(-)\text{-}DIOP]_2$, 30 ml absolute ethanol, 30 ml toluene, and 165 atm of hydrogen at 100°C for 8 h. The autoclave was cooled to room temperature and 10.2 g of a mixture in which 2-methylbutanoic acid was the only acid present was collected. It had an optical purity of 35.2%.

The mixture still remaining in the autoclave was transferred under pressure of hydrogen into a second similar autoclave containing 2.0 g of tiglic acid, the hydrogen pressure was adjusted to 130 atm, and the autoclave was kept at 100°C for 10 h. Cooling gave another sample (10.7 ml). The only acidic product present in this sample was (+)(*S*)-2-methylbutanoic acid, of optical purity 37.8%. Taking into account the amount of 2-methylbutanoic acid remaining in the autoclave after the first run, the stereoselectivity reached in the hydrogenation of tiglic acid in the second run was 51.2%.

Tiglic acid (2.0 g) was then hydrogenated by the same procedure described above after addition to the mixture in the autoclave left after the previous run. The optical purity of (+)(*S*)-2-methylbutanoic acid recovered at the end was 37.8%. The enantiomeric discrimination in this second re-use of the catalyst was 37.8%.

Hydrogenation of tiglic acid in the presence of (+)(S)-2-methylbutanoic acid

Tiglic acid (0.18 g), $\{Ru_2(CO)_4[(S)\text{-}(OOCCH(CH_3)C_2H_5]_2[(-)\text{-DIOP}]_2\}_m$ (34.8 mg), (+)(*S*)-2-methylbutanoic acid (0.58 g) (optical purity 98.9%), toluene (7.5 ml) and absolute ethanol (7.5 ml) were placed in the autoclave, and hydrogen was admitted to 130 atm. The autoclave was kept at 100°C for 5 h. Tiglic acid (1.63 g) was added in six portions through a liquid injector, each portion was dissolved in 5 ml of 1/1 toluene/ethanol, and the portions were added every 9 h.

GLC analysis indicated that total hydrogenation of the tiglic acid had occurred to give (+)(*S*)-2-methylbutanoic acid of 48.5% optical purity. Taking account of the fact that 0.58 g of the acid of 98.9% optical purity was initially introduced, the enantiomeric discrimination in the hydrogenation of tiglic acid with this procedure was 28.6%.

Hydrogenation of (+)-$\{Ru_2(CO)_4[OOCC(CH_3)=CHCH_3]_2[(-)\text{-DIOP}]\}_m$

A mixture of (+)-$\{Ru_2(CO)_4[(OOCCH(CH_3)=CHCH_3]_2[(-)\text{-DIOP}]\}_m$ (0.300 g), ethanol (10 ml), toluene (10 ml), and hydrogen (130 atm at 20°C) was kept at 100°C for 2 h in the autoclave. n-Pentanoic acid (1.5 g) was then added to the product mixture and the acidic material was recovered. The mixture of (+)(*S*)-2-methylbutanoic acid (1.3%) and n-pentanoic acid (98.7%) thus obtained had $\alpha_{D(l=1)}^{25}$ +0.22°, indicating an optical purity of 9.2% for the optically active acid.

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