Synthesis, Characterization, and Behavior of Hydridoruthenium Carbonyl Clusters Substituted with Functionalized Phosphines in the Presence of Hydrogen. 1. $H_4Ru_4(CO)_8[P(CH_2OCOR)_3]_4$ (R = CH_3-, C_2H_5-, $(CH_3)_2CH-$, $(CH_3)_3C-$, (*S*)-$C_2H_5CH(CH_3)-$)

Mario Bianchi,† Piero Frediani,† Antonella Salvini,† Luca Rosi,† Leonardo Pistolesi,† Franco Piacenti,*,† Sandra Ianelli,‡ and Mario Nardelli‡

Dipartimento di Chimica Organica della Università di Firenze, via Gino Capponi, 9, I50121 Firenze, Italy, and Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica e Chimica Fisica, della Università di Parma, Centro di Studio per la Strutturistica Diffrattometrica del CNR, Viale delle Scienze, 78, I43100 Parma, Italy

Received January 19, 1996⊗

The synthesis and characterization of phosphines containing ester groups $P(CH_2OCOR)_3$ (R = CH_3-, C_2H_5-, $(CH_3)_2CH-$, $(CH_3)_3C-$, (*S*)-$C_2H_5CH(CH_3)-$) are reported. The new hydridoruthenium complexes $H_4Ru_4(CO)_8[P(CH_2OCOR)_3]_4$ (R = CH_3-, C_2H_5-, $(CH_3)_2CH-$, $(CH_3)_3C-$, (*S*)-$C_2H_5CH(CH_3)-$) were synthesized and characterized. The structure of (+)-(*S*)-$H_4Ru_4(CO)_8\{P[CH_2OCOCH(CH_3)C_2H_5]_3\}_4$ was determined by X-ray diffraction. The behavior of these complexes in hydrocarbon solution with hydrogen under pressure (130 atm) in the temperature range 25−130 °C has been investigated. The ester groups present in the ligand $P(CH_2OCOR)_3$ are hydrogenated under mild conditions with formation of the corresponding alcohol RCH_2OH.

Introduction

Phosphines containing functionalized substituents have gained considerable interest in homogeneous catalysis by transition metals.[1,2] When used as ligands in metal complexes, they offer the possibility to tailor their solubility, reactivity, and activity and to serve as catalytic precursors or as reagents for special uses such as medical diagnostic materials.[3] The possibility of converting the functional groups in a phosphine provides an additional synthetic tool to elaborate new ligands. We have therefore synthesized several ligands of the type $P(CH_2OCOR)_3$ (R = CH_3-, C_2H_5-, $(CH_3)_2CH-$, $(CH_3)_3C-$, (*S*)-$C_2H_5CH(CH_3)-$) starting from $P(CH_2OH)_3$, a water-soluble, easily accessible phosphine, by esterification with appropriate carboxylic acid anhydrides.

Cluster hydridoruthenium carbonyl complexes containing ester ligands, $H_4Ru_4(CO)_8[P(CH_2OCOR)_3]_4$ (R = CH_3- (**1**), C_2H_5- (**2**), $(CH_3)_2CH-$ (**3**), $(CH_3)_3C-$ (**4**), (*S*)-$C_2H_5CH(CH_3)-$ (**5**)), were prepared and characterized with the aim of comparing their catalytic activity in the hydrogenation of both prochiral and achiral organic substrates with that of analogous complexes containing a chiral bidentate ligand, $H_4Ru_4(CO)_8[(-)\text{-DIOP}]_2$,[4,5] or a trialkylphosphine, $H_4Ru_4(CO)_8(PBu_3)_4$ (**6**).[6,7] The structure of **5** was determined by X-ray diffraction in order to determine the coordination mode of the phosphine, which, in principle, may act as a polydentate ligand. In consideration of the P−C bond hydrogenolysis suffered under hydrogenation conditions by the phosphine ligand in $H_4Ru_4(CO)_8(PBu_3)_4$[8] and $H_4Ru_4(CO)_8(PPh_3)_4$,[9] we have initially tested the behavior of the complexes prepared under hydrogen.

Results and Discussion

(a) Synthesis and Characterization of $P(CH_2OCOR)_3$ (R = CH_3-, C_2H_5-, $(CH_3)_2CH-$, $(CH_3)_3C-$, (*S*)-$C_2H_5CH(CH_3)-$). The above phosphines have been synthesized by reacting tris(hydroxymethyl)phosphine with the anhydride of the appropriate carboxylic acid in excess at temperatures between 25 and 80 °C (Scheme 1), following a slightly modified version of the procedure reported for the analogous tris(acetoxymethyl)phosphine.[10−12] Minor quantities of the monohydroxy and dihydroxy phosphines were still present at the end of the reaction. The desired phosphines were purified by distillation and characterized as $P(CH_2-$

† Università di Firenze.
‡ Università di Parma.
⊗ Abstract published in *Advance ACS Abstracts,* December 15, 1996.

(1) Sinou, D. *Bull. Soc. Chim. Fr.* **1987**, 480.
(2) Joo, F.; Toth, Z. *J. Mol. Catal.* **1980**, *8*, 369.
(3) (a) Hirth, W. W. *Diss. Abstr. Int. B* **1988**, *49*, 1657; *Chem. Abstr.* **1989**, *110*, 110926d. (b) Chiu, K. W.; Kelly, J. D.; Latham, I. A.; Griffiths, D. V.; Edwards, P. G. Eur. Pat. Appl. EP 311,352; *Chem. Abstr.* **1990**, *112*, 154491d. (c) Archer, C. M.; Dilworth, J. R.; Jobanputra, P.; Latham, I. A.; Thompson, R. M. PCT Int. Appl. WO 91 03,262; *Chem. Abstr.* **1991**, *115*, 239704n.
(4) Botteghi, C.; Gladiali, S.; Bianchi, M.; Matteoli, U.; Frediani, P.; Vergamini, P. G.; Benedetti, E. *J. Organomet. Chem.* **1977**, *140*, 221.
(5) Bianchi, M.; Matteoli, U.; Menchi, G.; Frediani, P.; Pratesi, S.; Piacenti, F.; Botteghi, C. *J. Organomet. Chem.* **1980**, *198*, 73.
(6) Frediani, P.; Bianchi, M.; Matteoli, U.; Menchi, G.; Petrucci, G. IV Simposio Italo-Cecoslovacco di Catalisi, Torino, Italy, Sept 20−23, 1983.
(7) Bianchi, M.; Menchi, G.; Francalanci, F.; Piacenti, F.; Matteoli, U.; Frediani, P.; Botteghi, C. *J. Organomet. Chem.* **1980**, *188*, 109.
(8) Salvini, A.; Frediani, P.; Bianchi, M.; Piacenti, F. JOM Conference '93, Monaco, Nov 4−5, 1993; p 150.
(9) Salvini, A. Unpublished results.
(10) Lanoux, S. B.; Ellzey, S. E., Jr.; Drake, G. L., Jr.; Reeves, W. A. U.S. Pat. 3,725,001; *Chem. Abstr.* **1973**, *79*, 93375v.
(11) Lanoux, S.; Drake, G. L., Jr. *Proc. La. Acad. Sci.* **1973**, *36*, 56; *Chem. Abstr.* **1975**, *82*, 31377.
(12) Mironova, Z. N.; Tsvetkov, E. N.; Nikolaev, A. V.; Kabachnik, M. I. *Zh. Obshch. Khim.* **1967**, *37*, 2747; *Chem. Abstr.* **1968**, *69*, 19262.

S0276-7333(96)00037-4 CCC: $14.00

Table 1. ^{1}H NMR Data for Ligands and Complexes[a]

compd	H−[Ru]	PCH_2OCO	OCOCH(CH_3)	CH_2OCOCH(CH_3)	CHC$H_2$$CH_3$	CHCH_2CH_3
P(CH_2OCOCH_3)$_3$		4.52, d, 2 H, $^2J_{HP}$ = 5.4	2.07, s, 3 H			
P($CH_2OCOC_2H_5$)$_3$		4.50, d, 2 H, $^2J_{HP}$ = 5.4	2.32, q, 2H, $^3J_{HH}$ = 7.6	1.10, t, 3 H, $^3J_{HH}$ = 7.6		
P[$CH_2OCOCH(CH_3)_2$]$_3$		4.52, d, 2 H, $^2J_{HP}$ = 5.2	2.57, sp, 1 H, $^3J_{HH}$ = 7.0	1.16, d, 6 H, $^3J_{HH}$ = 7.0		
P[$CH_2OCOC(CH_3)_3$]$_3$		4.49, d, 2 H, $^2J_{HP}$ = 5.1		1.19, s, 9 H		
(+)-(*S*)-P[$CH_2OCOCH(CH_3)C_2H_5$]$_3$[b]		4.54, d, 6H, J_{HP} = 4.8	2.41, m, 3H	1.07, d, 9H, J_{HH} = 7.0	1.45, m, 3H; 1.57, m, 3H	0.84, t, 9H, J_{HH} = 7.4
$H_4Ru_4(CO)_8$[P(CH_2OCOCH_3)$_3$]$_4$[c]	−17.96, qt, 4H, J_{HP} = 7.3	4.70, s, 2 H	2.11, s, 3 H			
$H_4Ru_4(CO)_8$[P($CH_2OCOC_2H_5$)$_3$]$_4$[d]	−17.49, qt, 4H, J_{HP} = 7.3	4.98, s, 2 H	2.17, q, 2 H, $^3J_{HH}$ = 7.5	0.98, t, 3 H, $^3J_{HH}$ = 7.5		
$H_4Ru_4(CO)_8$[P($CH_2OCOCH(CH_3)_2$)$_3$]$_4$[d]	−17.39, qt, 4H, J_{HP} = 7.2	5.06, s, 2 H	2.55, sp, 2 H, $^3J_{HH}$ = 7.0	1.11, d, 6 H, $^3J_{HH}$ = 7.0		
$H_4Ru_4(CO)_8$[P($CH_2OCOC(CH_3)_3$)$_3$]$_4$[d]	−17.25, qt, 4H, J_{HP} = 7.2	5.13, s, 2 H		1.22, s, 9 H		
(+)-(*S*)-$H_4Ru_4(CO)_8$[P($CH_2OCOCH(CH_3)C_2H_5$)$_3$]$_4$[d]	−17.34, m, 4H	5.10, q, 24H, J_{HP} = 14.2	2.47, q, 12H, J_{HH} = 6.7	1.13, d, 36H, J_{HH} = 6.6	1.72, m, 12H; 1.10, m, 12H	0.85, t, 36H, J_{HH} = 7.5

[a] $CDCl_3$ solvent. Chemical shifts are in ppm and coupling constants in Hz. Abbreviations: d, doublet; t, triplet; q, quartet; qt, quintet; sp, septuplet; m, multiplet; pq pseudoquartet; pt, pseudotriplet. [b] DMSO-d_6 solvent. [c] CD_2Cl_2 solvent. [d] C_6D_6 solvent.

Table 2. ^{13}C NMR Data for Ligands and Complexes[a]

compd	[Ru]−CO	PCH_2O	PCH_2OCO	OCOCH(CH_3)	OCOCH(CH_3)	CH$CH_2$$CH_3$	CH$CH_2$$CH_3$
P(CH_2OCOCH_3)$_3$[b]		58.7, d, $^1J_{CP}$ = 12.4	170.8, s	20.6, s			
P($CH_2OCOC_2H_5$)$_3$		58.6, d, $^1J_{CP}$ = 12.5	172.2, d, $^3J_{CP}$ = 2.6	27.3, s	9.0, s		
P[$CH_2OCOCH(CH_3)_2$]$_3$		58.6, d, $^1J_{CP}$ = 12.1	176.9, d, $^3J_{CP}$ = 2.6	33.9, s	19.0, s		
P[$CH_2OCOC(CH_3)_3$]$_3$		58.8, d, $^1J_{CP}$ = 11.5	178.2, d, $^3J_{CP}$ = 2.5	39.0, s	27.2, s		
(+)-(*S*)-P[$CH_2OCOCH(CH_3)C_2H_5$]$_3$[c]		58.5, d, J_{CP} = 11.4	175.6, s	*e*	16.3, s	26.2, s	11.2, s
$H_4Ru_4(CO)_8$[P(CH_2OCOCH_3)$_3$]$_4$[b]	197.7, m	61.8, t, J_{CP} = 13.8	170.4, s	20.6, s			
$H_4Ru_4(CO)_8$[P($CH_2OCOC_2H_5$)$_3$]$_4$[d]	199.2, m	61.7, t, J_{CP} = 13.6	173.3, s	27.1, s	8.9, s		
$H_4Ru_4(CO)_8$[P($CH_2OCOCH(CH_3)_2$)$_3$]$_4$[d]	198.2, m	61.8, t, J_{CP} = 13.6	176.0, s	34.0, s	19.0, s		
$H_4Ru_4(CO)_8$[P($CH_2OCOC(CH_3)_3$)$_3$]$_4$[d]	198.6, m	62.7, pt	177.8, s	39.6, s	27.6, s		
(+)-(*S*)-$H_4Ru_4(CO)_8$\{P[$CH_2OCOCH(CH_3)C_2H_5$]$_3$\}$_4$[d]	198.3, m	61.8, t, J_{CP} = 13.7	175.6, s	40.9, s	16.6, s	26.9, s	11.6, s

[a] $CDCl_3$ solvent. Chemical shifts are in ppm and coupling constants in Hz. Abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; pt, pseudotriplet. [b] CD_2Cl_2 solvent. [c] DMSO-d_6 solvent. [d] C_6D_6 solvent. [e] Masked by the solvent.

OCOR)$_3$ on the basis of their ^{1}H, ^{31}P, and ^{13}C NMR spectra (Tables 1−3) and GC-MS analyses (Table 4). Yields were always around 60%.

Scheme 1

$$P(CH_2OH)_3 + 3(RCO)_2O \rightarrow P(CH_2OCOR)_3 + 3RCOOH$$

$$R = CH_3-,\ C_2H_5-,\ (CH_3)_2CH-,\ (CH_3)_3C-,\ (S)\text{-}C_2H_5CH(CH_3)-$$

(b) Synthesis and Characterization of $H_4Ru_4(CO)_8[P(CH_2OCOR)_3]_4$ Complexes. The title complexes were prepared as described by Piacenti et al.[13] for the analogous tributylphosphine-substituted ruthenium complexes by reacting $H_4Ru_4(CO)_{12}$ with P(CH_2OCOR)$_3$ in *n*-heptane (Scheme 2). The ^{1}H, ^{31}P, and ^{13}C NMR and IR spectra (Tables 1−3 and 5) are in agreement with the structures reported in the literature for the analogous ruthenium complexes: a tetrahedral ruthenium cluster similar to that of $H_4Ru_4(CO)_{12}$[14] containing one phosphine per ruthenium atom. These

Table 3. ^{31}P NMR Data for Ligands and Complexes[a]

compd	δ (ppm)
P(CH_2OCOCH_3)$_3$	−30.6
P($CH_2OCOC_2H_5$)$_3$	−31.0
P[$CH_2OCOCH(CH_3)_2$]$_3$	−30.8
P[$CH_2OCOC(CH_3)_3$]$_3$	−30.6
(+)-(*S*)-P($CH_2OCOCH(CH_3)C_2H_5$)$_3$[b]	−30.0
$H_4Ru_4(CO)_8$[P(CH_2OCOCH_3)$_3$]$_4$[c]	24.5
$H_4Ru_4(CO)_8$[P($CH_2OCOC_2H_5$)$_3$]$_4$[d]	24.8
$H_4Ru_4(CO)_8$[P($CH_2OCOCH(CH_3)_2$)$_3$]$_4$[d]	24.5
$H_4Ru_4(CO)_8$[P($CH_2OCOC(CH_3)_3$)$_3$]$_4$[d]	23.4
(+)-(*S*)-$H_4Ru_4(CO)_8$[P($CH_2OCOCH(CH_3)C_2H_5$)$_3$]$_4$[d]	24.7

[a] $CDCl_3$ solvent. All signals shown are singlets. The chemical shifts (δ) are relative to external H_3PO_4 (85%); downfield values are assumed as positive. [b] DMSO-d_6 solvent. [c] CD_2Cl_2 solvent. [d] C_6D_6 solvent.

(13) Piacenti, F.; Bianchi, M.; Frediani, P.; Benedetti, E. *Inorg. Chem.* **1971**, *10*, 2759.

(14) (a) Bruce, M. I. In *Comprehensive Organometallic Chemistry*, 1st ed.; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1982; Vol. 4, p 889. (b) Wilson, R. D.; Wu, S. M.; Love, R. A.; Bau, R. *Inorg. Chem.* **1978**, *17*, 1271.

Table 4. Data for the Syntheses of Phosphines and Complexes

compd	reacn conditions: *T* (°C)	reacn conditions: time (h)	yield (%)	elemental anal.[a] (%): C	elemental anal.[a] (%): H	MS spectrum[b] (*m/e*)
$P(CH_2OCOCH_3)_3$	25	48	63.2	43.10 (43.21)	5.96 (6.04)	208, $[P(CH_2OCOCH_3)_2CH_2OH]^+$; 177, $[P(CH_2OCOCH_3)_2]^+$; 135, $[P(CH_2OCOCH_3)CH_2OH]^+$; 93, $[P(CH_2OH)_2]^+$; 73, $[CH_2OCOCH_3]^+$; 43 (100), $[CH_3CO]^+$
$P(CH_2OCOC_2H_5)_3$	40	24	75.0	49.35 (49.31)	7.30 (7.24)	236, $[P(CH_2OCOC_2H_5)_2(CH_2OH)]^+$; 235, $[P(CH_2OCOC_2H_5)_2(CH_2O)]^+$; 206, $[PH(CH_2OCOC_2H_5)_2]^+$; 205, $[P(CH_2OCOC_2H_5)_2]^+$; 149, $[P(CH_2OCOC_2H_5)(CH_2OH)]^+$; 148, $[P(CH_2OCOC_2H_5)(CH_2O)]^+$; 87, $[CH_2OCOC_2H_5]^+$; 57 (100), $[C_2H_5CO]^+$
$P[CH_2OCOCH(CH_3)_2]_3$	50	24	65.2	53.95 (53.89)	8.20 (8.14)	264, $[P[CH_2OCOCH(CH_3)_2]_2(CH_2OH)]^+$; 263, $[P[CH_2OCOCH(CH_3)_2]_2(CH_2O)]^+$; 247, $[P(CH_2OCOCH(CH_3)_2)_2(CH_2)]^+$; 234, $[PH(CH_2OCOCH(CH_3)_2)_2]^+$; 233, $[P(CH_2OCOCH(CH_3)_2)_2]^+$; 193, $[P(CH_2OCOCH(CH_3)_2)(CH_2OH)(CH_2O)]^+$; 177, $[P(CH_2OH)(CH_2OCOCH(CH_3)_2)(CH_2)]^+$; 163, $[P(CH_2OCOCH(CH_3)_2)(CH_2OH)]^+$; 71, $[(CH_3)_2CHCO]^+$; 43 (100), $[(CH_3)_2CH]^+$
$P[CH_2OCOC(CH_3)_3]_3$	50	48	58.1	57.25 (57.43)	8.76 (8.84)	262, $[PH(CH_2OCO(CH_3)_3)]^+$; 261, $[P(CH_2OCO(CH_3)_3)]^+$; 178, $[PH(CH_2OCO(CH_3)_3)(CH_2OH)]^+$; 177, $[P(CH_2OCOC(CH_3)_3)(CH_2OH)]^+$; 85, $[(CH_3)_3CCO]^+$; 57 (100), $[(CH_3)_3C]^+$
(+)-(*S*)-$P[CH_2OCOCH(CH_3)C_2H_5]_3$	80	96	60.0	56.85 (56.98)	9.50 (9.56)	376 (trace), $[M]^+$; 261 (24), $[M - CH_2OCOCH(CH_3)C_2H_5]$; 177 (44), $[P(CH_2OCOCH(CH_3)C_2H_5)(CH_2OH)]^+$; 85 (34), $[COCH(CH_3)C_2H_5]^+$; 57 (100), $[CH(CH_3)C_2H_5]^+$
$H_4Ru_4(CO)_8[P(CH_2OCOCH_3)_3]_4$	100	18	74.0	32.10 (32.36)	4.06 (3.95)	
$H_4Ru_4(CO)_8[P(CH_2OCOC_2H_5)_3]_4$	100	15	74.0	37.81 (37.34)	4.87 (4.92)	
$H_4Ru_4(CO)_8[P(CH_2OCOCH(CH_3)_2)_3]_4$	100	10	57.0	42.08 (41.46)	5.92 (5.73)	
$H_4Ru_4(CO)_8[P(CH_2OCOC(CH_3)_3)_3]_4$	100	7	77.0	44.08 (44.94)	6.70 (6.41)	
(+)(S)-$H_4Ru_4(CO)_8\{P[CH_2OCOCH(CH_3)C_2H_5)_3]_3\}_4$	100	12	80.0	53.02 (53.70)	6.43 (6.22)	

[a] Calculated values are given in parentheses. [b] Spectra obtained by GC−MS technique.

structures are in keeping with the presence of one singlet in the ^{31}P NMR spectra of **1**−**5** due to four magnetically equivalent phosphine ligands. At the same time the presence of only one multiplet in the hydrido region of the ^1H NMR spectra of **1**−**5** is in agreement with the high symmetry of its structure and with the presence of four magnetically equivalent hydridic hydrogens. The structure of **5** has been confirmed by X-ray diffraction.

Scheme 2

$$H_4Ru_4(CO)_{12} + 4P(CH_2OCOR)_3 \rightarrow H_4Ru_4(CO)_8(PCH_2OCOR)_4 + 4CO$$

1−**5**

R = CH_3- (**1**), C_2H_5- (**2**), $(CH_3)_2CH-$ (**3**), $(CH_3)_3C-$ (**4**), (*S*)-$C_2H_5CH(CH_3)-$ (**5**)

(c) Crystal-State Molecular Structure of $H_4Ru_4(CO)_8\{P[CH_2OCOCH(CH_3)C_2H_5]_3\}_4$. Figure 1 shows the ORTEP[16] drawing of the entire molecule, while Figure 2 shows the enlarged projection of the central core, giving a more clear view of the metal cluster and its nearest surroundings. The molecule is built from a central tetrahedral closed-shell 60-electron metal cluster, lying on a crystallographic 2-fold axis. If the phosphine groups are not considered, the local approximate symmetry is D_{2d}, with carbonyls and phosphines terminal. The coordination number about each ruthenium atom is 8 and involves three metal atoms, two carbonyls, one phosphine, and two bridging hydride hydrogens.

As explained in the Experimental Section, the phosphine chains are disordered; thus, their localization and shape are not well-defined. Nevertheless, Figure 1 gives a quite reliable image of their arrangement about the central core of the molecule. The relevant structural parameters concerning the central core of the molecule are compared by considering the two parts of the asymmetric unit in Table 6, where averaged values are also given. All the values are near those expected. It is relevant to note that, as found in other H_4Ru_4 hydrido clusters,[14b] there are two kinds of Ru−Ru distances, one shorter (average 2.784(5) Å) and the other longer (average 2.980(7) Å), corresponding to the edges unsubtended and subtended by the hydrido bridges, respectively, with a local idealized D_{2d} symmetry as found in the cluster of the precursor $H_4Ru_4(CO)_{12}$ and in that of the triphenylphosphine derivative $H_4Ru_4(CO)_{10}(PPh_3)_2$.[14b]

Table 5. IR Spectral Data for the Complexes in the 2200−1500 cm^{-1} region[a]

compd	ν(CO) (cm^{-1})	ν(OCOR) (cm^{-1})
$H_4Ru_4(CO)_8[P(CH_2OCOCH_3)_3]_4$	2022 (vs), 1984 (m), 1964 (s)	1752 (vs)
$H_4Ru_4(CO)_8[P(CH_2OCOC_2H_5)_3]_4$	2021 (vs), 1983 (m), 1963 (s)	1748 (vs)
$H_4Ru_4(CO)_8[P(CH_2OCOCH(CH_3)_2)_3]_4$	2021 (vs), 1984 (m), 1964 (s)	1748 (vs)
$H_4Ru_4(CO)_8[P(CH_2OCOC(CH_3)_3)_3]_4$	2022 (vs), 1983 (m), 1964 (s)	1737 (vs)
(+)-(*S*)-$H_4Ru_4(CO)_8\{P[CH_2OCOCH_2CH(CH_3)C_2H_5]_3\}_4$[b]	2023 (vs), 1986 (m), 1967 (vs)	1751 (s)

[a] CH_2Cl_2 solvent. Abbreviations: vs, very strong; s, strong; m, medium. [b] *n*-Pentane solvent.

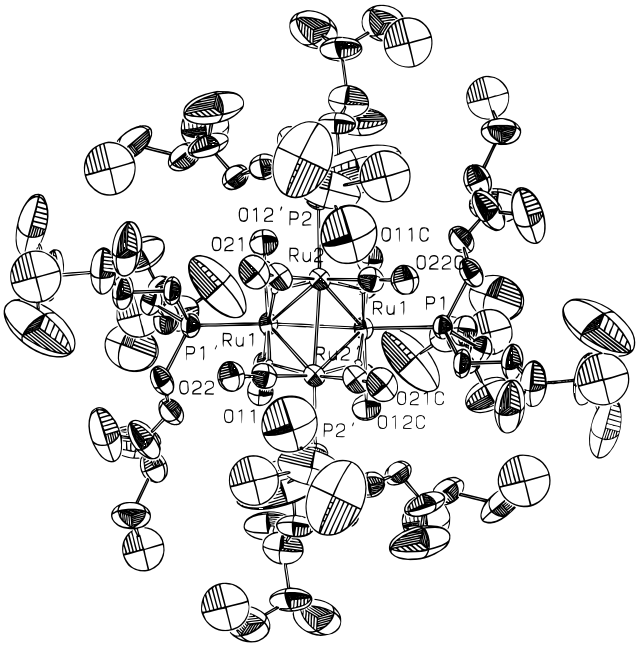


Figure 1. (+)-(*S*)-$H_4Ru_4(CO)_8\{P[CH_2OCOCH(CH_3)C_2H_5]_3\}_4$: ORTEP projection of the structure of the entire molecule along the 2-fold axis. For the sake of clarity the hydrogen atoms and many of the atom labels are omitted. Ellipsoids are shown at the 30% probability level.

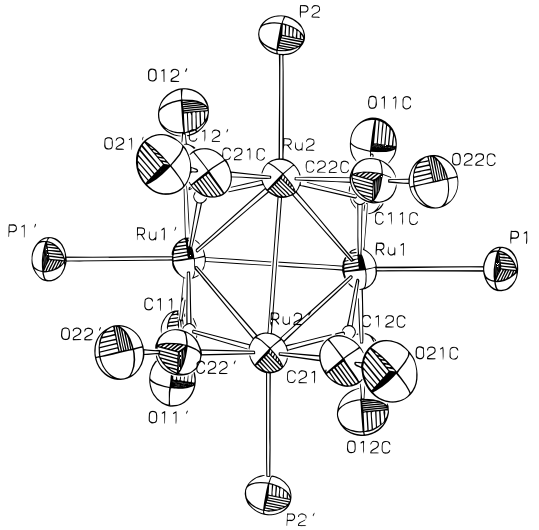


Figure 2. (+)-(*S*)-$H_4Ru_4(CO)_8\{P[CH_2OCOCH(CH_3)C_2H_5]_3\}_4$: ORTEP projection of the central core of the molecule along the 2-fold axis. Ellipsoids are shown at the 30% probability level.

(d) Behavior of Ruthenium Complexes under Hydrogen. The behavior of these new complexes under hydrogen has been investigated by following the evolution of the system in hydrocarbon solution under 130 atm of hydrogen at selected temperatures in the range 25−150 °C. Samples of the solution, taken from the pressure reactor, were analyzed by GC and GC−MS in order to detect the presence of organic products due to a modification of the phosphinic ligand and by IR and TLC techniques for organometallic species. All complexes remain practically unchanged up to 100 °C. At this temperature, new bands begin to appear in the carbonyl stretching region of the IR spectra. The analysis of the sample by GC and GC−MS shows the presence of the corresponding alcohols RCH_2OH due to the reduction of the carboxylic acid engaged as ester in the phosphinic ligand. CH_3OCOR esters, which would eventually be formed in the hydrogenolysis of the P−C bond, were not detected, although very careful analyses were performed.

The amount of alcohol formed increases in all cases when the reaction temperature is increased (Table 7): at 130 °C almost one-third of the ester groups present in the phosphine ligands are reduced. At this temperature, a very complex IR pattern in the 2200−1200 cm^{-1} region is indicative of the presence in solution of a mixture of ruthenium complexes, among which the presence of the starting complex cannot be confirmed. The band at 1748 cm^{-1}, with an intensity lower than that of the initial solution, is indicative of the partial reduction of the ester groups present in the ligands, in keeping with the GC indications of the presence of alcohol.

A precipitate is also formed (30−50% of the starting complex). Its IR spectrum (KBr pellets) shows absorptions in the carbonyl stretching region (2200−1800 cm^{-1}) and a strong, broad band centered at 3500 cm^{-1}, which is in keeping with the presence of ruthenium complexes containing (hydroxymethyl)phosphines. The characterization of these complexes by spectroscopic methods is not possible, due to their very low solubility in organic solvents. The above results indicate that the phosphines tested, when present as ligands in the ruthenium complexes, do not undergo, in the presence of hydrogen under pressure, hydrogenolysis of the P−C bond, in contrast to the trialkyl- or triarylphosphine.[8,9] Their esteric groups, however, are easily reduced even under mild conditions (Scheme 3). This behavior is rather surprising, considering the difficulty generally encountered in the reduction of the esters of carboxylic acids, at least of the monoesters,[7] to alcohols in the homogeneous phase. Esters of aliphatic acids are in fact unaffected by hydrogen under 200 atm at 220 °C in the presence of $H_4Ru_4(CO)_8(PBu_3)_4$ (**6**). They, on the other hand, may be reduced (90 °C, 6 atm of hydrogen), although with low conversions, using anionic hydridoruthenium derivatives as catalysts as a result of a believed nucleophilic hydride transfer process.[15]

(15) Grey, R. A.; Pez, G. P.; Wallo, A. *J. Am. Chem. Soc.* **1981**, *106*, 7536.

(16) Johnson, C. K. ORTEP; Report ORNL-3794; Oak Ridge National Laboratory, Oak Ridge, TN, 1965.

Table 6. Comparison of Relevant Bond Distances (Å) and Angles (deg) for (+)-(*S*)-$H_4Ru_4(CO)_8\{P(CH_2OCOCH(CH_3)C_2H_5)_3\}_4$[a]

bond or angle		bond or angle		av
Ru1−Ru1′	2.779(2)	Ru2−Ru2′	2.790(2)	2.784(5)
Ru1−Ru2	2.973(1)	Ru1−Ru2′	2.988(1)	2.980(7)
Ru1−P1	2.310(3)	Ru2−P2	2.296(3)	2.303(7)
Ru1−C11C	1.858(11)	Ru2−C21C	1.851(11)	
Ru1−C12C	1.872(12)	Ru2−C22C	1.845(12)	1.855(4)
P1−C1	1.825(13)	P2−C19	1.814(15)	
P1−C7	1.834(13)	P2−C25	1.816(12)	1.826(5)
P1−C13	1.833(12)	P2−C31	1.830(14)	
O11C−C11C	1.161(13)	O21C−C21C	1.156(15)	
O12C−C12C	1.126(14)	O22C−C22C	1.169(15)	1.153(9)
Ru2−Ru1−Ru2′	55.8(0)	Ru1−Ru2−Ru1′	55.6(0)	55.7(10)
Ru1′−Ru1−Ru2′	61.9(0)	Ru1′−Ru2−Ru2′	61.8(0)	61.8(5)
Ru1′−Ru1−Ru2	62.5(0)	Ru1−Ru2−Ru2′	62.4(0)	62.4(5)
Ru2′−Ru1−P1	110.6(1)	Ru1−Ru2−P2	112.8(1)	111.7(11)
Ru2−Ru1−P1	106.5(1)	Ru1′−Ru2−P2	109.2(1)	107.8(14)
Ru1′−Ru1−P1	168.7(1)	Ru2′−Ru2−P2	170.9(1)	169.8(11)
P1−Ru1−C12C	95.3(3)	P2−Ru2−C22C	95.5(4)	95.4(10)
P1−Ru1−C11C	93.8(3)	P2−Ru2−C21C	92.8(4)	93.4(5)
Ru1−P1−C1	119.8(4)	Ru2−P2−C31	119.1(4)	119.4(4)
Ru1−P1−C7	115.1(4)	Ru2−P2−C19	115.9(4)	115.5(4)
Ru1−P1−C13	117.7(4)	Ru2−P2−C25	118.1(4)	117.9(3)
Ru2−Ru1−C11C	106.5(3)	Ru1′−Ru2−C21C	105.9(3)	106.2(3)
Ru2−Ru1−C12C	151.3(4)	Ru1′−Ru2−C22C	147.4(4)	149(2)
Ru1′−Ru1−C11C	92.0(3)	Ru2′−Ru2−C21C	90.6(4)	91.5(7)
Ru1′−Ru1−C12C	94.3(3)	Ru1−Ru2−C22C	95.7(4)	94.8(7)
Ru2′−Ru1−C11C	152.7(3)	Ru1−Ru2−C21C	151.8(4)	152.4(4)
Ru2′−Ru1−C12C	99.4(3)	Ru2′−Ru2−C22C	92.6(4)	97(3)
Ru1−C11C−O11C	178.3(9)	Ru2−C21C−O21C	175.8(10)	
Ru1−C12C−O12C	178.6(10)	Ru2−C22C−O22C	177.5(11)	177.6(6)
C11C−Ru1−C12C	89.9(5)	C21C−Ru2−C22C	93.5(5)	92(2)
C1−P1−C7	100.6(6)	C19−P2−C25	100.0(6)	
C1−P1−C13	101.1(5)	C25−P2−C31	100.4(6)	100.2(3)
C7−P1−C13	99.3(5)	C19−P2−C31	99.9(6)	
P1−C1−O1	107.7(9)	P2−C19−O7	114.2(11)	
P1−C7−O3	108.9(8)	P2−C25−O9	110.3(8)	109.3(9)
P1−C13−O5	107.0(8)	P2−C31−O11	109.9(9)	

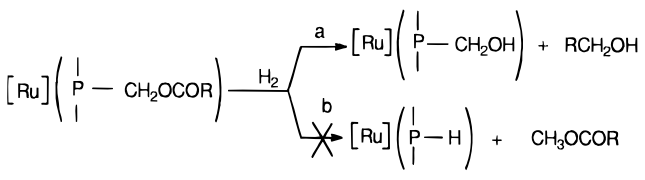
[a] Esd's are given in parentheses. A slanted prime indicates the symmetry operation *x*, 2−y, 2−z.

Table 7. Behavior of $H_4Ru_4(CO)_8[P(CH_2OCOR)_3]_4$ (1−5) with Hydrogen: Hydrogenation of the Ester Group Present in the Coordinated Phosphine[a]

			ester group reduced to alcohol (%)					
compd	R	hydrogenated product	80 °C	100 °C	110 °C	120 °C	130 °C	130 °C[c]
1	CH_3−	CH_3CH_2OH	n.d.	n.d.	n.d.	n.d.	26	n.d.
2	CH_3CH_2−	$CH_3CH_2CH_2OH$	trace	7.0	9	18	37	n.d.
3	$(CH_3)_2CH$−	$(CH_3)_2CHCH_2OH$	trace	4	7	17	34	n.d.
4	$(CH_3)_3C$−	$(CH_3)_3CCH_2OH$	trace	4	15	33	36	n.d.
5	(*S*)-$CH_3CH_2CH(CH_3)$−[b]	(−)-(*S*)-$CH_3CH_2CH(CH_3)CH_2OH$		trace	n.d.	n.d.	12	16

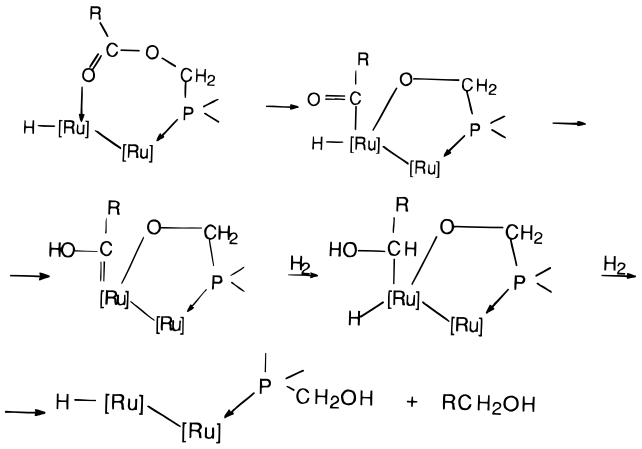
[a] Conditions: solvent benzene (5 mL); complex (10.6 μmol); $p(H_2)$ 130 atm; reaction time 24 h. [b] $p(H_2)$ 50 atm; solvent *n*-heptane (5 mL). [c] Reaction time 48 h.

Scheme 3



The reactivity of the ester group in the phosphine used as ligand in the present complexes seems to depend, to some extent, on the structure of the esteric group in the phosphine ligand: phosphines containing bulky alkoxy groups (i.e. *tert*-butyl) appear in fact to be the most reactive (Table 7). The easier activation of the ester group when engaged in a phosphine present as a ligand in a hydridometal cluster such as $H_4Ru_4(CO)_8[P(CH_2OCOR)_3]_4$ might be connected to a more facile preliminary coordination to a metal center, not necessarily the same one bound to the phosphine. The reduction would then occur via oxidative addition of the RC(═O)OC group to the metal with formation of an acylic species, which is then converted to alcohol through known steps (Scheme 4). We must stress, however, that while RCH_2OH species are formed by hydrogenation of the acyl group in the ligand, no evidence has been obtained (at room temperature), neither by X-ray diffraction nor by NMR spectroscopy, for the behavior of such a phosphine as a bidentate ligand.

Scheme 4



Experimental Section

Instruments. Gas chromatographic analyses (GC) were performed with a Perkin-Elmer Sigma 1 system or a Shimadzu GC-14A chromatographic system coupled with a Shimadzu C-R4A computer; the packed columns (2 m) used were PPG ("Polypropylenglicol" LB-550-X on Chromosorb W at 15%), FFAP ("free fatty acids phase" on Chromosorb G AW-DMCS at 5%), and OV1 (silicone on Chromosorb G AW-DMCS at 2.5%). Both apparatus were equipped with an FID. The determinations of the amount of alcohols were made using a calibration curve. GC−MS spectra were collected using a Shimadzu GC-MS-QP2000 instrument or a Carlo Erba QMD 1000 GC−MS data system equipped with capillary columns: either an SPB-1 (a Supelco column, 30 m, internal diameter 0.25 mm) or an AT-1 (Alltech column, 30 m, internal diameter 0.25 mm). Infrared spectra were recorded with an FTIR spectrophotometer, Perkin-Elmer Model 1760-X. Liquid products and solutions were analyzed using a KBr or a CaF_2 cell having a 0.1 mm path. Solid samples were mulled with KBr.

Multinuclear NMR spectra were acquired using a Varian VXR300 spectrometer operating at 299.944 MHz for ^{1}H, at 75.429 MHz for ^{13}C, and at 121.421 MHz for ^{31}P NMR spectra; tetramethylsilane was used as external reference for ^{1}H and ^{13}C NMR spectra. In the ^{31}P NMR spectra, values downfield from external H_3PO_4 (85%) were taken as positive. ^{13}C and ^{31}P NMR spectra were recorded as proton-decoupled spectra. Optical rotations were measured with a Perkin-Elmer 241 polarimeter.

Materials. Reagents and solvents were purified and dried as reported. *n*-Heptane was purified by treatment with concentrated H_2SO_4 and then with $KMnO_4$ in 10% H_2SO_4 solution and then dried on anhydrous $CaCl_2$, refluxed over sodium, and distilled from $LiAlH_4$. Methanol, dried as reported by Vogel,[17] had bp 65 °C. Diethyl ether was refluxed and distilled on $LiAlH_4$. (−)-(*S*)-2-Methylbutanol had bp 128 °C, $[\alpha]^{25}_D = -5.82°$, and optical purity 100%.[18] Acetic propanoic, 2-methylpropanoic, and 3,3-dimethylpropanoic anhydrides were commercial products and were distilled prior to use. All other solvents and chemicals were reagent grade and were used with no further purification.

All reactions and manipulations were performed under dry nitrogen by the Schlenk tube technique. $P(CH_2OH)_3$ was synthesized and purified as reported in the literature.[19,20] (+)-(*S*)-2-Methylbutanoic acid was prepared and purified as reported in the literature:[21,22] bp 76−77 °C/16 mmHg and $[\alpha]^{25}_D = +19.7°$. The optical purity of the acid was 99.5%, assuming $[\alpha]^{25}_D(\max) = +19.8°$ and $d^{25}_4 = 0.9313$.[22] (+)-(*S*)-2-Methylbutanoyl chloride,[23] synthesized and purified as reported by Vogel[17] for analogous compounds, had bp 116−117 °C. (+)-(*S*)-2-Methylbutanoic anhydride,[24] synthesized and purified as reported by Vogel[17] for analogous compounds, had bp 89−90 °C/23 mmHg and $[\alpha]^{25}_D = +34.0°$. The (+)-(*S*)-2-methylbutanoic acid recovered after hydrolysis of the anhydride catalyzed by H_2SO_4 at room temperature and the usual workup had $[\alpha]^{25}_D = +18.3°$ (optical purity 90.6%[22]). $H_4Ru_4(CO)_{12}$ was synthesized as reported by Piacenti et al.[25]

Synthesis of $P(CH_2OCOR)_3$. As an example, the synthesis of (+)-(*S*)-$P[CH_2OCOCH(CH_3)C_2H_5]$ is reported. The reaction conditions and the data for all syntheses are reported in Table 4. A suspension of 1.5 g of $P(CH_2OH)_3$ (12.09 mmol) in 6.7 g of (+)-(*S*)-2-methylbutanoic anhydride (35.97 mmol) was stirred in a 20 mL Schlenk tube under nitrogen for 96 h at 80 °C. The reaction was monitored by IR spectroscopy and GC analyses using an OV1 column at 38 °C for 20 min and then heated to 280 °C at a rate of 10 °C/min and kept at this temperature for 15 min. At the end of the reaction, the (+)-(*S*)-2-methylbutanoic acid formed and the residual (+)-(*S*)-2-methylbutanoic anhydride were removed by distillation under reduced pressure. The colorless residue was distilled under high vacuum (bp 143 °C/5.4 × 10^{-5} mbar), and 2.73 g (7.25 mmol) of phosphine (60% yield) was obtained. The purified phosphine had $[\alpha]^{25}_D = +22.2°$ (c = 5.01, $CHCl_3$). The spectroscopic data are reported in Tables 1−3. The mass spectrum, determined by GC−MS analysis using the AT-1 column kept at 100 °C for 2 min, heated to 300 °C at a rate of 10 °C/min, and then kept at this temperature for 20 min, is reported in Table 4.

Synthesis of the Ruthenium Complexes $H_4Ru_4(CO)_8[P(CH_2OCOR)_3]_4$ (1−5). As an example, the synthesis of (+)-(*S*)-$H_4Ru_4(CO)_8\{P[CH_2OCOCH(CH_3)C_2H_5]_3\}_4$ is reported. The reaction conditions and the data for all syntheses are reported in Table 4. In a 50 mL round-bottom flask, $H_4Ru_4(CO)_{12}$ (0.110 g, 0.148 mmol), $P(CH_2OCOR)_3$ (0.055 g, 0.444 mmol), and 10 mL of *n*-heptane were introduced under nitrogen. The mixture was heated to 90 °C for 24 h; the CO formed in the reaction was removed by bubbling nitrogen through the mixture. The course of the reaction was monitored by IR spectroscopy and TLC. The IR spectrum of the solution showed a complex pattern. This pattern remained unaltered after further warming. The main product present in the solution was separated by preparative TLC on silica gel using a diethyl ether−light petroleum ether (bp 40−60 °C) (1:3) mixture as eluant. Red crystals were obtained from *n*-pentane at −20 °C. After two recrystallizations 0.206 g of complex (78% yield) was obtained. The purified complex had mp 65−66 °C and $[\alpha]^{25}_D = +15.5°$ (c = 0.88, C_6H_6). The spectroscopic data of the complexes synthesized are reported in Tables 1−3 and 5.

X-ray Crystallography. The relevant data for the crystal structure analysis of **5** are summarized in Table 8. The lattice parameters were determined with Mo Kα radiation (λ =

(17) Vogel, A. *Vogel's Textbook of Practical Organic Chemistry*, 4th ed.; Longmans: London, 1978.
(18) (a) Rossi, R.; Diversi, P.; Ingrosso, G. *Gazz. Chim. Ital.* **1968**, *98*, 1391. (b) Lardicci, L.; Menicagli, R. *Atti Soc. Toscana Sci. Nat. Pisa, Mem., Ser. A* **1970**, *77*, 25.
(19) Sasse, K. In *Methoden der Organischen Chemie*; Houben-Weil, Eds.; George Thieme Verlag: Stuttgart, Germany, 1963; Vol. XII/1, p 28.
(20) Reuter, M.; Orthner, L. Ger. Offen. 1,035,135 (1958): *Chem. Abstr.* **1960**, *54*, 14124i.
(21) von Freudenberg, K.; Lwowski, W. *Justus Liebigs Ann. Chem.* **1955**, *594*, 76.
(22) Lardicci, L.; Botteghi, C.; Belgodere, E. *Gazz. Chim. Ital.* **1967**, *97*, 610.
(23) (a) Kharasch, M. S.; Kuderna, J.; Nudenberg, W. *J. Org. Chem.* **1954**, *19*, 1283. (b) Weisenborn, F. L.; Bolger, J. W.; Rosen, D. B.; Mann, L. T., Jr.; Johnson, L.; Holmes, H. L. *J. Am. Chem. Soc.* **1954**, *76*, 1792.
(24) (a) Wang, N.-Y.; Hsu, C.-T.; Sih, C. J. *J. Am. Chem. Soc.* **1981**, *103*, 6538. (b) Hsu, C.-T.; Wang, N.-Y.; Latimer, L. H.; Sih, C. J. *J. Am. Chem. Soc.* **1983**, *105*, 593.
(25) Piacenti, F.; Bianchi, M.; Frediani, P.; Benedetti, E. *Inorg. Chem.* **1971**, *10*, 2759.

Table 8. Experimental Data for the X-ray Analysis of (+)-(*S*)-$H_4Ru_4(CO)_8\{P(CH_2OCOCH(CH_3)C_2H_5)_3\}_4$

formula	$C_{80}H_{136}O_{32}P_4Ru_4$
M_r	2138.04
space group[a]	$P22_12_1$
a/Å	12.696(2)
b/Å	14.544(8)
c/Å	28.202(23)
V/Å^3	5208(5)
Z	2
D_{exptl}/Mg m^{-3}	1.364
$F(000)$	2216
cryst size/mm	0.26 × 0.29 × 0.35
μ/mm^{-1}	0.701
θ range for intensity collection/deg	3.0/26.1
hkl ranges	−15 to +15; 0−17; 0−34
std refln	076
intensity variation/%	<0.1
no. of measd rflns	10 103
no. of unique rflns	9585
R(int)	0.0363
no. of rfls used in the refinement (N)	9585
no. of rflns with $I > 2\sigma(I)$	4934
no. of refined params (PR)	524
max LS shift to esd ratio	−0.081
min/max height in final $\Delta\rho$ map/e Å^{-3}	−0.34/+0.42
$wR2 = [\sum w(\Delta F^2)^2/\sum w(F_o^2)^2]^{1/2}$	0.1516
$S = [\sum w(\Delta F^2)^2/(N - PR)]^{1/2}$	1.051
$R1 = \sum\|\Delta F\|/\sum\|F_o\|$ for $I > 2\sigma(I)$	0.0565
$R1$ for all data	0.1702
Flack param	−0.11(6)
weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0565P)^2 + 6.7389P]$, where $P = (F_o^2 + 2F_c^2)/3$

[a] Unconventional setting of the space group No. 18 with equivalent positions: x, y, z; $x, -y, -z$; $-x, {}^1/_2 + y, {}^1/_2 - z$; $-x, {}^1/_2 - y, {}^1/_2 + z$.

0.710 73 Å) and refined by a least-squares procedure,[26] using the Nelson and Riley[27] extrapolation function, on 29 reflections in the θ range 10−15°. The integrated intensities were measured at room temperature (293(2) K) on an Enraf-Nonius CAD4 diffractometer with Mo Kα radiation, using the $\theta-2\theta$ scan mode with a 3−12°/min scan speed, $1.2 + 0.35 \tan\theta$ scan width and a modified version[28] of the Lehmann and Larsen[29] peak-profile analysis procedure. All reflections were corrected for Lorentz and polarization effects; no correction for absorption was considered.

The structure was solved by the direct methods of SHELXS-86,[30] which gave the heaviest atoms and a number of oxygen and carbon atoms; the other non-hydrogen atoms were then found from successive difference Fourier maps. Refinement, carried out by full-matrix least squares on F^2 using the SHELXL-93[31] program, was difficult because of the disorder affecting the phosphine hydrocarbon chains and also some of the oxygen atoms. In spite of this disorder, the hydride hydrogens were found in the difference maps and refined isotropically, giving Ru−H distances ranging from 1.50(9) to 1.83(9) Å and angles Ru1−H1R−Ru2′ = 132(3)° and Ru1−H2R−Ru2 = 126(6)°. The other hydrogen atoms, when possible, were placed in calculated positions; owing to disorder, particularly of the methyl and ethyl groups, the hydrogens of these groups could not be considered. Considering the final atomic coordinates of non-H atoms given in the Supporting Information, it must be pointed out that, for some chain disordered atoms, these parameters have no meaning other than that of contributions to improve the agreement between the observed and calculated structure factors. The most relevant structural parameters of the two parts of the asymmetric unit are compared in Table 6, where the C−C and C−O distances and angles of the phosphine chains are not considered, since they are not reliable. When averaging is meaningful, the averaged values are also given.

The absolute configuration was assigned on the basis of the Flack[32] index, giving an unequivocal answer, in spite of the fact that the intensity data were from Mo radiation.

All calculations were carried out on the ENCORE-91 and POWERNODE-6040 computers of the "Centro di Studio per la Strutturistica Diffrattometrica del CNR (Parma)". In addition to the quoted programs, PARST[33] was used for the calculations concerning the geometrical aspects of the crystal structures.

Atomic scattering factors and anomalous-scattering coefficients were taken from ref 34. Fractional coordinates for all atoms, bond lengths, bond angles, and torsional angles are available as Supporting Information and have been deposited at the Cambridge Crystallographic Data Centre.

Behavior of Ruthenium Complexes under Hydrogen. General Procedure. The experiments on the reactivity of ruthenium complexes were carried out in a glass vial placed in a stainless steel rocking autoclave (150 mL). In the glass vial, under dry nitrogen, the ruthenium complex (10.6 μmol) and 5 mL of solvent were introduced. The autoclave was then sealed and hydrogen added up to 130 atm at 20 °C. The autoclave was placed in a thermostated oil bath set at the desired temperature (±1 °C) and rocked for 24 h. After the mixture was cooled to room temperature, the gas was vented and samples of the reaction solution were collected and analyzed by GC, IR, and GC−MS.

RCH_2OH was present in solution, as shown by the GC and GC−MS analyses. The quantitative determinations were obtained by GC analyses using calibration curves obtained from solutions of known composition. GC analyses were

(26) Nardelli, M.; Mangia, A. *Ann. Chim. (Rome)* **1984**, *74*, 163.
(27) Nelson, J. B.; Riley, D. P. *Proc. Phys. Soc., London* **1945**, *57*, 160, 477.
(28) Belletti, D.; Ugozzoli, F.; Cantoni, A.; Pasquinelli, G. Internal Report 1-3/79; Centro di Studio per la Strutturistica Diffrattometrica del CNR, Parma, Italy, 1979.
(29) Lehmann, M. S.; Larsen, F. K. *Acta Crystallogr., Sect. A* **1974**, *30*, 580.
(30) Sheldrick, G. M. SHELXS-86, Program for Crystal Structure Solution; University of Göttingen, Göttingen, Germany, 1986.
(31) Sheldrick, G. M. SHELXL-93, Program for Crystal Structure Refinement; University of Göttingen, Göttingen, Germany, 1992.
(32) Flack, H. D. *Acta Crystallogr., Sect. A* **1983**, *39*, 876.
(33) Nardelli, M. *Comput. Chem.* **1983**, *7*, 95.
(34) International Union of Crystallography. *International Tables for Crystallography*; Kluwer Academic: Dordrecht, The Netherlands, 1992; Vol. C, Tables 4.2.6.8, 6.1.1.4.

performed as follows: CH_3CH_2OH, a FFAP column heated to 50 °C for 30 min; $CH_3CH_2CH_2OH$, a PPG column heated to 50 °C for 25 min and then heated to 90 °C at a rate of 3 °C/min and kept at this temperature for 10 min; $(CH_3)_2CHCH_2OH$, a PPG column heated to 35 °C for 35 min and then heated to 90 °C at a rate of 10 °C/min and kept at this temperature for 10 min; $(CH_3)_3CCH_2OH$, a PPG column heated to 50 °C for 25 min and then heated to 90 °C at a rate of 3 °C/min and kept at this temperature for 10 min; $C_2H_5CH(CH_3)CH_2OH$, an OV1 column heated to 40 °C for 20 min and then heated to 280 °C at a rate of 10 °C/min and kept at this temperature for 10 min or an FFAP column heated to 45 °C for 10 min and then heated to 140 °C at a rate of 10 °C/min and kept at this temperature for 30 min.

GC−MS analyses were performed using a SPB-1 capillary column kept at 35 °C for 15 min and then heated to 250 °C at a rate of 15 °C/min and kept at this temperature for 25 min. MS spectra of RCH_2OH are in agreement with those reported in the literature.[35]

Acknowledgment. We thank the Ministero della Ricerca Scientifica e Tecnologica (MURST) for financial support.

Supporting Information Available: Tables of atomic coordinates, thermal parameters, bond distances and angles, and torsion angles for (+)-(*S*)-$H_4Ru_4(CO)_8[P(CH_2OCOCH(CH_3)C_2H_5)_3]_4$ (9 pages). Ordering information is given on any current masthead page.

OM960037L

(35) *EPA/NIH Mass Spectral Data Base*; Heller, S. R., Milne, G. W. A., Eds.; U.S. Department of Commerce, National Bureau of Standards: Washington, DC, 1978.