Synthesis and Structural Characterization of the Tetraruthenium Cluster Complexes $[Ru_4(\mu\text{-}H)_4(CO)_{10}(L\text{–}L)]$ (L–L = diphosphine) *

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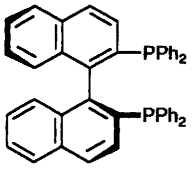
The clusters $[Ru_4(\mu\text{-}H)_4(CO)_{10}\{(S)\text{-}(-)\text{-binap}\}]$ **1** and $[Ru_4(\mu\text{-}H)_4(CO)_{10}\{(S)\text{-}(-)\text{-mobiph}\}]$ **2** containing the atropoisomeric diphosphine ligands (*S*)-(−)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (binap) and (*S*)-(−)-2,2′-bis(diphenylphosphino)-6,6′-dimethoxy-1,1′-biphenyl (mobiph) have been synthesized *via* direct reaction of $[Ru_4H_4(CO)_{12}]$ in toluene at 150 °C with a two-fold excess of the diphosphine under hydrogen pressure. Their molecular and crystal structures have been determined by single-crystal X-ray diffraction: both crystallize in the orthorhombic system, space group $P2_12_12_1$, $Z = 4$; $a = 13.009(7)$, $b = 14.357(2)$, $c = 29.109(7)$ Å for **1**; $a = 12.108(8)$, $b = 15.845(3)$, $c = 28.241(5)$ Å for **2**. In both complexes the diphosphine ligand chelates the Ru atom involved in three hydride bridges.

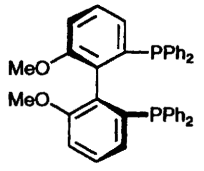
Excellent results have been obtained in a variety of asymmetric hydrogenations using homogeneous catalysts based on mononuclear ruthenium complexes co-ordinated by atropoisomeric diphosphine ligands such as (*S*)-(−)-binap [(*S*)-(−)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl][1] or (*S*)-(−)-mobiph [(*S*)-(−)-2,2′-bis(diphenylphosphino)-6,6′-dimethoxy-1,1′-biphenyl].[2] To the best of our knowledge, no corresponding polynuclear ruthenium species have been tested, even though clusters such as $[Ru_4H_4(CO)_8\{(-)\text{-(diop)}\}_2]$ {(−)-diop = (−)-(4*R*,5*R*)-4,5-bis[(diphenylphosphino)methyl]-2,2-dimethyl-1,3-dioxolane} gave good results in asymmetric reactions such as hydrogenations, isomerizations and hydroformylations.[3] Therefore, we thought it interesting to study the reactivity of $[Ru_4H_4(CO)_{12}]$ in the presence of (*S*)-(−)-binap or (*S*)-(−)-mobiph in an attempt to synthesize some new hydrido-ruthenium clusters to be used in asymmetric catalysis.

In this paper we report the synthesis and characterization of two new hydrido clusters $[Ru_4H_4(CO)_{10}(L\text{–}L)]$ where L–L is (*S*)-(−)-binap or (*S*)-(−)-mobiph. The structures of the two complexes in the solid state have been determined by single-crystal X-ray diffraction.

Results and Discussion

Synthesis and Spectroscopic Characterization.—It is known that stepwise substitution of CO groups in $[Ru_4H_4(CO)_{12}]$ by monodentate tertiary phosphines L gives the corresponding $[Ru_4H_4(CO)_{12-n}L_n]$ clusters,[4] the major product of the reaction being determined by the phosphorus to ruthenium molar ratio. The reaction of $[Ru_4H_4(CO)_{12}]$ with bidentate diphosphine ligands can afford di- or tetra-substitution of the CO ligands. An example of a disubstituted cluster is $[Ru_4H_4(CO)_{10}(dppe)]$ [dppe = 1,2-bis(diphenylphosphino)ethane][5] which exists in two isomeric forms, one with the diphosphine chelating only one ruthenium atom, the other with it bridging one of the Ru–Ru edges. A systematic study of the influence of the aliphatic chain length on the bridge–chelate isomerization process as well as a full structural characterization has also been reported in the cases of the derivatives $[Ru_4H_4(CO)_{10}\{Ph_2P(CH_2)_nPPh_2\}]$ ($n = 1$ or 3–5) and $[Ru_4H_4(CO)_{10}\{Ph_2PCH_2CH(Me)PPh_2\}]$.[6] The asymmetric diphosphine (−)-diop gives tetrasubstituted species of formula $[Ru_4H_4(CO)_8\{(-)\text{-diop}\}_2]$[7] with the two diphosphines spanning two different Ru–Ru edges.[8]


(*S*)-(−)-binap



(*S*)-(−)-mobiph

In our case, with both diphosphines the reaction does not proceed beyond disubstitution even in the presence of an excess of the diphosphine and under forcing conditions. Thus, $[Ru_4H_4(CO)_{12}]$ reacts in toluene at 150 °C with a two-fold excess of (*S*)-(−)-binap or (*S*)-(−)-mobiph under hydrogen pressure to give as the main product a red compound which can be formulated as $[Ru_4H_4(CO)_{10}(L\text{–}L)]\cdot$solv [L–L = (*S*)-(−)-binap, solv = CH_2Cl_2 **1**; L–L = (*S*)-(−)-mobiph, solv = heptane **2**]. The formation of these clusters is always accompanied by the presence of small amounts of another polynuclear species not having hydrido ligands (as inferred by IR and ^1H NMR spectroscopy) the characterization of which is still in progress.

Both compounds **1** and **2** exhibit seven major absorptions in the CO region of the IR spectrum in hexane solution (**1**, 2070vs, 2040vs, 2020vs, 2000vs, 1990s, 1980s, 1970s; **2**, 2075vs, 2040vs, 2018s, 2000s, 1982s, 1970s, 1958vs cm^{-1}) indicating that these species have low molecular symmetry and are structurally correlated.

More direct evidence on the nature of compounds **1** and **2** can be obtained from NMR spectroscopy. At room temperature the ^1H NMR spectra show the presence of broad resonances in the hydrido region. Hydrido clusters of the type $[Ru_4H_4(CO)_{12-n}L_n]$ are dynamic on the NMR time-scale owing to fluxional motions involving the hydride ligands.[5,6] In our case such exchange processes are relatively slow since static spectra are obtained at ≈253 K for **1** and at ≈273 K for **2**, respectively.

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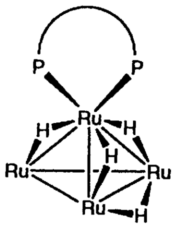
* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

The low-temperature patterns observed for the hydrides confirm that the two species have essentially the same structure {**1**, δ −16.56 (s), −17.05 (t) [*J*(P–H) = 13], −16.68 (dd) [*J*(H–P) = 18.1 and 32.8], −17.60 (dd) [*J*(H–P) = 20.9 and 30.1]; **2**, δ −16.53 (s), −17.21 (t) [*J*(P–H) = 14], −16.70 (dd) [*J*(H–P) = 19 and 34] and −17.60 (dd) [*J*(H–P) = 20 and 31 Hz]}. Moreover, the ^{31}P NMR spectra consist of AB spin systems [**1**, δ_A = 38.99, δ_B = 28.72, *J*(P–P) = 26.7; **2**, δ_A = 40.47, δ_B = 31.58, *J*(P–P) = 27.1 Hz] therefore suggesting a structure such as that depicted in **I**, in which the diphosphine ligand chelates the apical ruthenium atom of the tetrahedral cluster with the hydrides spanning the ruthenium–ruthenium edges. Indeed both the ^1H and the ^{31}P NMR spectra closely resemble those of $[Ru_4H_4(CO)_{10}(dppe)]$.[5] As in this latter case, there is a strict agreement between the lowest-temperature ^1H NMR spectra of **1** and **2** and the H(hydride) distribution inferred on the basis of the diffraction study (see below). Therefore, the structures frozen out in the solid state coincide with the ground-state distribution of the H(hydride) ligands in solution. It should be mentioned that the alternative way of distributing the H(hydrides), namely that of idealized D_{2d} symmetry, has been observed only in the precursor $[Ru_4H_4(CO)_{12}]$ and in the phosphine derivative $[Ru_4H_4(CO)_{10}(PPh_3)_2]$[9] where the H atoms span two edges of each triangular face.

The Solid-state Molecular Structures of Compounds **1** *and* **2**.—The structures of both compounds **1** and **2** were established by X-ray crystallographic studies and are shown in Figs. 1 and 2, respectively, together with their atomic labelling. Relevant structural parameters are reported in Table 1. While previous crystal structures of metal complexes containing the binap ligand are known,[10] this is the first structural report on a (*S*)-(−)-mobiph metal cluster. Both species contain a distorted-tetrahedral core of Ru atoms where the 'basal' atoms preserve the tricarbonyl units of the parent $[Ru_4H_4(CO)_{12}]$[9] and the 'apical' atom, Ru(1), is bound to only one CO group and carries a diphosphine ligand bound in a chelating mode. The electronic



I

Table 1 Bond distances (Å) and angles (°) for compounds **1** and **2**

	1		2
Ru(1)–Ru(2)	2.997(2)		3.008(1)
Ru(1)–Ru(3)	3.027(2)		3.045(1)
Ru(1)–Ru(4)	3.007(2)		2.987(1)
Ru(2)–Ru(3)	2.766(2)		2.770(1)
Ru(2)–Ru(4)	2.773(2)		2.769(1)
Ru(3)–Ru(4)	2.920(2)		2.947(1)
Ru(1)–P(1)	2.331(3)		2.331(3)
Ru(1)–P(2)	2.360(4)		2.359(3)
P(1)–C(23)	1.85(1)		1.86(1)
P(2)–C(34)	1.85(1)	P(2)–C(31)	1.84(1)
C(23)–C(32)	1.40(2)	C(23)–C(28)	1.37(2)
C(32)–C(33)	1.49(2)	C(28)–C(30)	1.52(2)
C(33)–C(34)	1.38(2)	C(30)–C(31)	1.41(2)
		C(27)–O(12)	1.35(2)
		O(12)–C(29)	1.41(2)
		C(35)–O(11)	1.37(2)
		O(11)–C(36)	1.40(2)
Ru–C (CO) mean	1.89_2		1.90_3
C–O (CO) mean	1.13_1		1.13_2
P(1)–Ru(1)–P(2)	93.8(1)		93.5(1)
Ru(1)–P(1)–C(23)	108.2(4)		111.5(3)
C(23)–C(32)–C(33)	124(1)	C(23)–C(28)–C(30)	125(1)
C(32)–C(33)–C(34)	126(1)	C(28)–C(30)–C(31)	125(1)
C(33)–C(34)–P(2)	121(1)	C(30)–C(31)–P(2)	122(1)
C(34)–P(2)–Ru(1)	118.2(4)	C(31)–P(2)–Ru(1)	116.5(4)
		C(27)–O(12)–C(29)	118(1)
		C(35)–O(11)–C(36)	119(1)

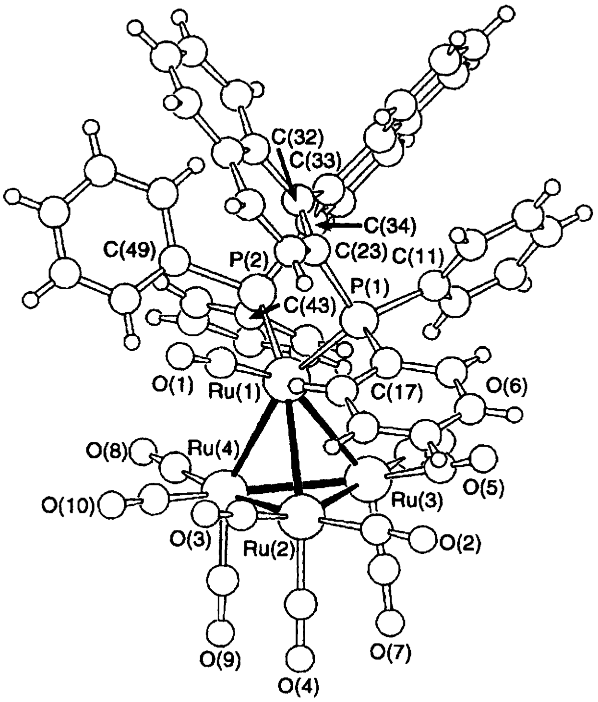


Fig. 1 Solid-state molecular structure of compound **1** showing the atom labelling scheme

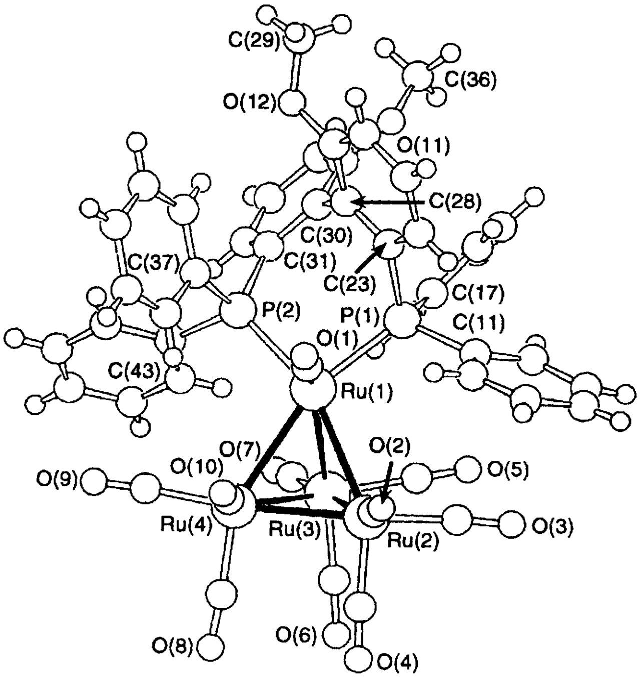


Fig. 2 Solid-state molecular structure of compound **2** showing the atom labelling scheme

requirements of both clusters are completed by four bridging hydride atoms, the majority of which could not be located directly (see Experimental section). The Ru–Ru bond lengths, however, provide good indications of their locations: in both complexes four 'long' [Ru(1)–Ru(2) 2.997(2), 3.008(1) Å; Ru(1)–Ru(3) 3.027(2), 3.045(1) Å; Ru(1)–Ru(4) 3.007(2), 2.987(1) Å; Ru(3)–Ru(4) 2.920(2), 2.947(1) Å in **1** and **2** respectively] and two 'short' distances [Ru(2)–Ru(3) 2.766(2), 2.770(1); Ru(2)–Ru(4) 2.773(2), 2.769(1) Å in **1** and **2** respectively] are present, though not significantly different between the two species. The distribution of the H(hydride) atoms conforms to the idealized C_s symmetry of the tetrahedral core, bridging four edges, three of which belong to the same triangular face. The same distribution has been observed for all diphosphine derivatives of [$Ru_4H_4(CO)_{12}$] thus far reported.[5,6] In both **1** and **2** the Ru atom carrying the chelating ligand belongs to the H-bridged triangular face and is involved in three bridges. The H(hydride) distribution in both species leads to the formation of the same diastereomer.

Both the diphosphine ligands have known *S* chirality, which

Table 2 Crystal data and details of measurements for compounds **1** and **2***

	1	**2**
Formula	$C_{54}H_{36}O_{10}P_2Ru_4 \cdot CH_2Cl_2$	$C_{48}H_{36}O_{12}P_2Ru_4 \cdot C_7H_{16}$
M	1396.0	1371.2
Crystal size/mm	0.25 × 0.17 × 0.32	0.12 × 0.2 × 0.28
a/Å	13.009(7)	12.108(8)
b/Å	14.357(2)	15.845(3)
c/Å	29.109(7)	28.241(5)
U/Å^3	5436(2)	5418(2)
F(000)	2736	2728
μ(Mo-Kα)/cm^{-1}	13.0	12.1
θ range (°)	2.5–27	2.5–25
Measured reflections	6602	5311
Unique observed reflections [$I_o > 2\sigma(I_o)$]	4062	4351
No. of refined parameters	437	453
Goodness of fit on F^2	1.07	1.27
R on F, wR_2 on F^2	0.0518, 0.178	0.0386, 0.149
(all data)	(0.0985, 0.199)	(0.0651, 0.183)

* Details in common: 293 K; orthorhombic, space group $P2_12_12_1$; $Z = 4$; ω scan width 0.9°; $R(F) = \Sigma||F_o| - |F_c||/\Sigma(F_o)$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$.

Table 3 Atomic coordinates (× 10^4) for compound **1**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru(1)	3 316(1)	3 982(1)	1 247(1)	C(22)	3 595(11)	3 384(9)	−13(5)
Ru(2)	1 923(1)	2 411(1)	978(1)	C(23)	4 950(10)	5 129(9)	534(4)
Ru(3)	1 024(1)	3 907(1)	1 422(1)	C(24)	5 523(11)	4 623(10)	214(5)
Ru(4)	2 375(1)	2 609(1)	1 904(1)	C(25)	6 577(12)	4 680(11)	214(5)
P(1)	3 560(2)	4 889(2)	592(1)	C(26)	7 103(11)	5 264(10)	540(5)
P(2)	4 184(3)	5 037(3)	1 733(1)	C(27)	8 169(13)	5 333(12)	545(6)
O(1)	5 224(10)	2 891(10)	997(4)	C(28)	8 663(14)	5 921(13)	835(6)
O(2)	909(9)	2 697(9)	39(4)	C(29)	8 098(13)	6 494(12)	1 119(6)
O(3)	3 576(15)	1 134(12)	635(6)	C(30)	7 056(12)	6 457(11)	1 113(5)
O(4)	341(17)	928(13)	1 140(6)	C(31)	6 517(11)	5 843(10)	837(5)
O(5)	535(9)	4 595(9)	466(4)	C(32)	5 426(9)	5 767(8)	831(4)
O(6)	−20(11)	5 506(12)	1 917(5)	C(33)	4 856(11)	6 445(9)	1 122(5)
O(7)	−866(11)	2 694(13)	1 525(5)	C(34)	4 361(10)	6 251(9)	1 530(4)
O(8)	2 970(15)	2 952(12)	2 902(4)	C(35)	3 963(13)	6 982(10)	1 791(5)
O(9)	722(14)	1 235(13)	2 171(6)	C(36)	3 997(14)	7 884(12)	1 629(6)
O(10)	3 934(14)	1 100(11)	1 750(5)	C(37)	4 429(11)	8 097(10)	1 217(5)
C(1)	4 516(13)	3 338(11)	1 101(5)	C(38)	4 437(16)	9 036(15)	1 036(7)
C(2)	1 310(12)	2 605(12)	380(5)	C(39)	4 850(15)	9 217(15)	621(7)
C(3)	2 946(15)	1 615(12)	774(5)	C(40)	5 329(12)	8 494(11)	353(5)
C(4)	945(18)	1 498(15)	1 105(7)	C(41)	5 311(12)	7 636(11)	517(5)
C(5)	709(11)	4 326(11)	823(5)	C(42)	4 873(10)	7 397(9)	943(4)
C(6)	403(12)	4 913(13)	1 755(6)	C(43)	3 537(11)	5 201(10)	2 281(5)
C(7)	−164(14)	3 148(15)	1 476(7)	C(44)	2 525(13)	5 518(11)	2 282(6)
C(8)	2 714(16)	2 867(12)	2 533(6)	C(45)	2 055(17)	5 708(14)	2 694(7)
C(9)	1 336(15)	1 758(15)	2 059(6)	C(46)	2 539(17)	5 572(15)	3 101(8)
C(10)	3 371(15)	1 666(11)	1 789(5)	C(47)	3 532(18)	5 238(15)	3 116(8)
C(11)	2 952(9)	6 032(9)	532(4)	C(48)	4 014(15)	5 098(12)	2 707(6)
C(12)	2 220(12)	6 337(11)	839(5)	C(49)	5 475(10)	4 681(9)	1 913(5)
C(13)	1 795(14)	7 213(12)	793(6)	C(50)	6 248(13)	5 339(13)	1 988(6)
C(14)	2 070(15)	7 780(14)	436(6)	C(51)	7 200(18)	5 030(15)	2 146(7)
C(15)	2 790(14)	7 471(14)	108(6)	C(52)	7 383(16)	4 109(13)	2 191(6)
C(16)	3 208(14)	6 600(11)	163(6)	C(53)	6 627(16)	3 449(14)	2 125(6)
C(17)	3 217(10)	4 263(8)	53(4)	C(54)	5 685(12)	3 725(11)	1 977(5)
C(18)	2 515(12)	4 665(11)	−252(5)	Cl(1)	10 261(13)	8 017(10)	2 016(4)
C(19)	2 200(13)	4 137(11)	−621(6)	C(55)	10 247(23)	9 046(12)	1 694(9)
C(20)	2 576(14)	3 278(13)	−696(6)	Cl(2)	9 401(14)	8 829(9)	1 239(7)
C(21)	3 290(13)	2 871(12)	−398(5)				

Table 4 Atomic coordinates ($\times 10^4$) for compound **2**

Atom	*x*	*y*	*z*
Ru(1)	1580(1)	5019(1)	5874(1)
Ru(2)	3644(1)	4559(1)	5340(1)
Ru(3)	2113(1)	5540(1)	4862(1)
Ru(4)	1698(1)	3753(1)	5092(1)
P(1)	2036(2)	6134(2)	6376(1)
P(2)	−319(2)	5091(2)	6056(1)
O(1)	2056(8)	3797(6)	6652(4)
O(2)	4667(12)	3364(9)	6046(5)
O(3)	5467(8)	5859(7)	5462(4)
O(4)	4862(9)	3801(10)	4512(5)
O(5)	3503(10)	7066(7)	5106(4)
O(6)	3393(10)	5161(8)	3960(4)
O(7)	365(10)	6522(9)	4319(5)
O(8)	2671(12)	2927(9)	4213(4)
O(9)	−550(9)	3009(8)	4866(5)
O(10)	2350(11)	2374(7)	5773(5)
O(11)	−417(8)	7679(5)	7185(4)
O(12)	−1253(7)	6098(6)	7536(3)
C(1)	1842(9)	4273(7)	6366(4)
C(2)	4266(11)	3791(9)	5777(6)
C(3)	4766(10)	5370(9)	5431(5)
C(4)	4371(11)	4100(10)	4798(5)
C(5)	3005(11)	6491(9)	5027(4)
C(6)	2928(11)	5293(9)	4324(5)
C(7)	957(12)	6143(9)	4528(5)
C(8)	2333(12)	3256(9)	4545(5)
C(9)	236(11)	3317(8)	4951(5)
C(10)	2141(13)	2892(9)	5516(6)
C(11)	3553(9)	6185(7)	6478(4)
C(12)	4109(10)	5472(8)	6625(4)
C(13)	5230(12)	5488(10)	6708(5)
C(14)	5831(14)	6215(10)	6637(5)
C(15)	5284(13)	6925(10)	6466(5)
C(16)	4140(10)	6921(8)	6404(4)
C(17)	1671(9)	7239(7)	6240(4)
C(18)	1821(10)	7838(8)	6581(5)
C(19)	1574(13)	8664(10)	6488(5)
C(20)	1099(14)	8899(11)	6053(6)
C(21)	938(13)	8312(9)	5730(6)
C(22)	1201(11)	7459(8)	5805(5)
C(23)	1421(8)	5995(6)	6973(3)
C(24)	2084(10)	5741(7)	7350(4)
C(25)	1609(11)	5598(7)	7792(4)
C(26)	511(10)	5712(7)	7852(5)
C(27)	−155(10)	5972(7)	7491(4)
C(28)	311(9)	6118(7)	7036(4)
C(29)	−1667(13)	6329(13)	7983(6)
C(30)	−465(9)	6513(7)	6675(4)
C(31)	−841(9)	6119(7)	6256(4)
C(32)	−1579(10)	6539(7)	5972(4)
C(33)	−1945(12)	7343(8)	6081(5)
C(34)	−1569(11)	7753(8)	6482(4)
C(35)	−829(10)	7334(7)	6776(4)
C(36)	−750(15)	8491(8)	7314(6)
C(37)	−804(9)	4311(7)	6482(4)
C(38)	−1544(10)	4506(8)	6835(4)
C(39)	−1978(12)	3855(9)	7111(5)
C(40)	−1702(12)	3026(9)	7031(5)
C(41)	−971(12)	2829(9)	6660(5)
C(42)	−532(10)	3458(7)	6392(5)
C(43)	−1236(9)	4845(6)	5562(4)
C(44)	−2147(12)	4288(8)	5596(5)
C(45)	−2792(13)	4127(9)	5212(5)
C(46)	−2589(13)	4503(9)	4794(6)
C(47)	−1740(12)	5079(9)	4751(5)
C(48)	−1090(11)	5240(8)	5130(5)
C(50)	5409(24)	9681(16)	6827(9)
C(51)	4915(18)	8980(14)	7134(8)
C(52)	5539(19)	8369(14)	7457(9)
C(53)	4801(19)	7735(14)	7724(8)
C(54)	5351(21)	7006(16)	7992(10)
C(55)	4483(22)	6639(17)	8333(11)
C(56)	4986(20)	5926(16)	8632(10)

allows one to deduce the absolute configuration of compounds **1** and **2**. The resulting skewed seven-membered ring is then forced by the steric requirements of the diphosphine to adopt a λ conformation. The bite angles of the (*S*)-(−)-binap and (*S*)-(−)-mobiph ligands are very similar [93.8(1) and 93.5(1)°] and fall at the upper end of the range of values usually found for binap ligands in complexes of lower nuclearity.[10] The dihedral angles between the two naphthyl units in **1** and the two methoxyphenyl units in **2** are 76.3(3) and 68.4(3)° respectively. The Ru–P distances in the two species are unusually asymmetric [Ru(1)–P(1) 2.331(3) and 2.331(3) Å, Ru(1)–P(2) 2.360(4) and 2.359(3) Å in **1** and **2** respectively], though identical between the two sets of bonds. All the carbonyl groups are terminally bound, with Ru–C distances ranging from 1.85(1) to 1.93(2) Å.

Experimental

The diphosphine ligands (*S*)-(−)-binap[11] and (*S*)-(−)-mobiph[12] and the cluster $[Ru_4H_4(CO)_{12}]$[4b] were prepared as described in the literature. Elemental analyses were carried out at the University of Florence. Infrared spectra were obtained on a Perkin-Elmer 683 spectrophotometer, NMR spectra with a Bruker AC 200 spectrometer in $CDCl_3$ or CD_2Cl_2 solutions. Optical rotations were measured with a Perkin-Elmer 241 polarimeter. Values of $[\alpha]_D$ are given as 10^{-1} ° cm^2 g^{-1}.

Synthesis of Complexes.—(−)-$[Ru_4H_4(CO)_{10}\{(S)$-(−)-(binap)$\}]\cdot CH_2Cl_2$ **1**. A deaerated solution of $[Ru_4H_4(CO)_{12}]$ (0.436 g, 0.58 mmol) and binap (0.766 g, 1.23 mmol) in toluene (30 cm^3) was transferred to a stainless-steel autoclave (volume ≈ 150 cm^3) equipped with a magnetic stirring bar. The autoclave was pressurized to 150 bar (1.5×10^7 Pa) with hydrogen and heated to 150 °C. After 6 h the reactor was cooled to room temperature and the gas phase vented off. Thin-layer chromatographic analysis on silica gel (hexane–CH_2Cl_2 1 : 1) of the resulting red solution revealed the presence of two species. Recrystallization from CH_2Cl_2–MeOH afforded $[Ru_4H_4(CO)_{10}(binap)]\cdot CH_2Cl_2$ as red crystals (0.20 g, 26% yield) (Found: C, 47.05; H, 3.00. Calc. for $C_{55}H_{38}Cl_2O_{10}P_2Ru_4$: C, 47.25; H, 2.90%); $[\alpha]_D^{25}$ −440 (*c* 0.05 g cm^{-3}, CH_2Cl_2).

(−)-$[Ru_4H_4(CO)_{10}\{(S)$-(−)-mobiph$\}]\cdot C_7H_{16}$ **2**. This complex was synthesized analogously and recrystallized from CH_2Cl_2–MeOH–C_7H_{16} as red crystals (66% yield) (Found: C, 48.25; H, 3.55. Calc. for $C_{55}H_{52}O_{12}P_2Ru_4$: C, 48.20; H, 3.80%); $[\alpha]_D^{25}$ −395 (*c* 0.21 g cm^{-3}, CH_2Cl_2).

X-Ray Crystallography.—Diffraction data were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator (Mo-Kα radiation, λ = 0.710 69 Å). The intensities were collected in the ω–2θ scan mode at room temperature. Crystal data and details of measurements are summarized in Table 2. Both structures were solved by direct methods, followed by Fourier-difference syntheses and subsequent least-squares refinement. For all calculations the SHELX 86[13a] and SHELXL 93[13b] programs were used. Absorption corrections were applied by azimuthal scans of eight (**1**) and seven (**2**) reflections with $\chi > 80°$ (transmission range 0.75–1.00). Anisotropic thermal vibrations were applied to the $Ru_4(CO)_{10}$ core, including the MeO units in **2**. Owing to the better quality of the data for **2**, two hydride atoms could be located in Δ*F* maps, *i.e.* the ones bridging the Ru(1)–Ru(3) and Ru(3)–Ru(4) edges with Ru–H distances ranging from 1.67 to 1.80 Å. The H atoms of the phenyl and methyl groups were added in calculated positions (C–H 0.93 and 0.96 Å for the phenyl and methyl ones, respectively), and refined 'riding' on their respective C atoms. The absolute configurations of **1** and **2** were tested by using the Flack parameter [$-0.05(9)$ and $-0.14(7)$, respectively]. Both species cocrystallize with solvent molecules: **1** includes a disordered CH_2Cl_2 molecule, **2** a heptane one. Fractional atomic coordinates are reported in Tables 3 and 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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References

1 R. Noyori and H. Takaya, *Acc. Chem. Res.*, 1990, **23**, 345; T. Manimaran, T. Wu, W. D. Klobucar, C. H. Kolich, G. P. Stahly, F. R. Fronczek and S. E. Watkins, *Organometallics*, 1993, **12**, 1467; J. B. Hoke, L. S. Hollis and E. W. Stern, *J. Organomet. Chem.*, 1993, **455**, 193.

2 B. Heiser, E. A. Broger and Y. Crameri, *Tetrahedron Asymmetry*, 1991, **2**, 51.

3 U. Matteoli, P. Frediani, M. Bianchi, C. Botteghi and S. Gladiali, *J. Mol. Catal.*, 1981, **12**, 281; U. Matteoli, M. Bianchi, P. Frediani, G. Menchi, C. Botteghi and M. Marchetti, *J. Organomet. Chem.*, 1984, **263**, 243; F. Piacenti, P. Frediani, U. Matteoli, G. Menchi and M. Bianchi, *Chim. Ind.* (*Milan*), 1986, **68**, 53.

4 (*a*) G. Wilkinson, F. G. A. Stone and E. W. Abel (Editors), *Comprehensive Organometallic Chemistry*, Pergamon, New York, 1982, vol. 4, p. 891; (*b*) F. Piacenti, M. Bianchi, P. Frediani and E. Benedetti, *Inorg. Chem.*, 1971, **10**, 2759.

5 J. R. Shapley, S. I. Richter, M. R. Churchill and R. A. Lashewycz, *J. Am. Chem. Soc.*, 1977, **99**, 7384; M. R. Churchill, R. A. Lashewycz, J. R. Shapley and S. I. Richter, *Inorg. Chem.*, 1980, **19**, 1277.

6 J. Puga, A. Arce, D. Braga, N. Centritto, F. Grepioni, R. Castillo and J. Ascanio, *Inorg. Chem.*, 1987, **26**, 867.

7 C. Botteghi, M. Bianchi, E. Benedetti and U. Matteoli, *Chimia*, 1975, **29**, 256; C. Botteghi, S. Gladiali, M. Bianchi, U. Matteoli, P. Frediani, P. G. Vergamini and E. Benedetti, *J. Organomet. Chem.*, 1977, **140**, 221.

8 V. Gramlich, personal communication.

9 R. D. Wilson, S. M. Wu, R. A. Love and R. Bau, *Inorg. Chem.*, 1978, **17**, 1271.

10 M. T. Ashby, M. A. Khan and J. Halpern, *Organometallics*, 1991, **10**, 2011; H. Kawano, T. Ikariya, Y. Ishii, T. Kodama, M. Saburi, S. Yoshikawa, Y. Uchida and S. Akutagawa, *Bull. Chem. Soc. Jpn.*, 1992, **65**, 1595; K. Mashima, T. Hino and H. Takaya, *J. Chem. Soc., Dalton Trans.*, 1992, 2099 and refs. therein.

11 H. Takaya, S. Akutagawa and R. Noyori, *Org. Synth.*, 1988, **67**, 20.

12 R. Schmid, J. Foricher, M. Cereghetti and P. Schönholzer, *Helv. Chim. Acta*, 1991, **74**, 370.

13 G. M. Sheldrick, (*a*) *Acta Crystallogr., Sect. A*, 1990, **46**, 467; (*b*) SHELXL 93, University of Göttingen, 1993.

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