Towards a Library of "Early-Late" Ti–Ru Bimetallic Complexes

Laurianne Bareille,[a] Pierre Le Gendre,*[a] Philippe Richard,[a] and Claude Moïse*[a]

Keywords: Heterometallic complexes / Metallocenes / Ruthenium / Titanium

A series of new titanocene phosphanes **3**–**6** have been prepared by replacing both chloride atoms at the titanium atom of the complexes [$TiCl_2(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_4(CH_2)_2PR_2\}$] (**1**: R = Ph; **2**: R = Cy) by sodium fluoride or sodium benzoate in two-phase systems. Treatment of these new metalloligands with the binuclear complex [(*p*-cymene)$RuCl_2]_2$ affords the targeted titanocene difluoride and titanocene dibenzoate bimetallic ruthenium complexes **8**–**11**. The first chiral Ti–Ru bimetallic complex **12** bearing a binaphthyloxy ligand at the titanium centre has been synthesised in this way. In each series, an X-ray crystal structure has been determined.

Introduction

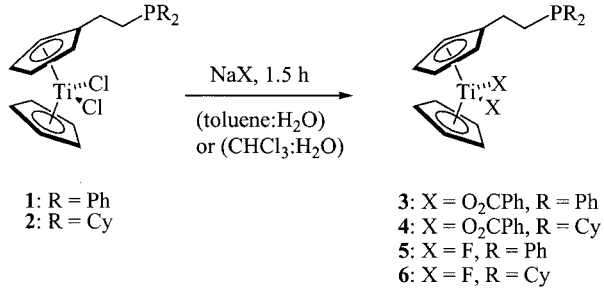
Complexes containing early as well as late transition metals are particularly attractive materials owing to their potential application in homogeneous catalysis.[1–3] Indeed, the coordination of the substrate to one of the two metals may increase its reactivity towards the other. Such compounds, which often show a cooperative effect, may constitute a new class of catalysts that are able to improve the efficiency of known processes or to give new reactions. Nevertheless, probably because of their laborious access, only a few early–late bimetallic complexes have been tested in catalysis.[4] Our strategy to construct such systems was to first synthesise a titanocene dichloride phosphane complex and then to treat these early metal ligands with the binuclear complex [(*p*-cymene)$RuCl_2]_2$.[5] We obtained a series of Ti–Ru heterobimetallic complexes in sufficient amounts to carry out a screening of their catalytic behaviour.[6–8] Another aspect of interest of this approach is the structural flexibility of the titanocene phosphane as regards a possible tuning of the bimetallic complexes towards the target catalytic reaction. Indeed, by replacing the two chloride atoms on the titanium atom by other ligands it should be possible to design new phosphanes and therefore to expand substantially this class of bimetallic complexes. Here we report the synthesis and the characterisation of a series of new Ti–Ru bimetallic complexes by using this strategy.

Results and Discussion

Titanocene dibenzoate can be synthesised, in good yields, from the reaction of titanocene dichloride with sodium benzoate in a biphasic system ($CHCl_3/H_2O$).[9] Therefore we carried out the reaction with the titanocene dichloride phosphanes **1** and **2** under similar conditions (Scheme 1). The colour of the reaction mixture, initially red, turned slowly to orange. After this treatment, titanocene dibenzoate phosphanes **3** and **4**, respectively, were isolated as orange powders in good yields. The NMR spectroscopic data of **3** and **4** are very similar to their dichloride counterparts **1** and **2**, with additional resonances for the benzoate hydrogens. The IR spectra exhibit two (COO) stretching bands around 1630 and 1320 cm^{-1}, consistent with the monodentate coordination of the benzoate ligands.[10] Thus, in one step, both the steric and electronic features of the titanocene phosphanes **1** and **2** have been modified. In an extension of this procedure, we conducted a reaction between sodium fluoride and the titanocene dichloride phosphanes **1** and **2** under similar conditions. The halide exchange proceeded smoothly and led to the titanocene difluoride phosphanes **5**, and **6**, respectively, in very good yields. The $^{19}F\{^1H\}$ NMR spectrum of **5** shows singlets at δ = 64.3 ppm in the range reported for [Cp_2TiF_2].[11] The $^{19}F\{^1H\}$ NMR spectrum of **6** also contains a singlet but with a chemical shift shifted slightly downfield at δ = 86.8 ppm. All other NMR spectroscopic data of **5** and **6** are in accordance with their structural features. At this point we should mention that [Cp_2TiF_2] has recently been converted, under mild conditions, into [Cp_2TiH], which has proved to be a very effective catalyst for the hydrosilylation of lactones[12] and the dehydropolymerisation of silanes.[13] The potential of the bimetallic complexes constructed with the fluorinated titanocene phosphane is thus reinforced.

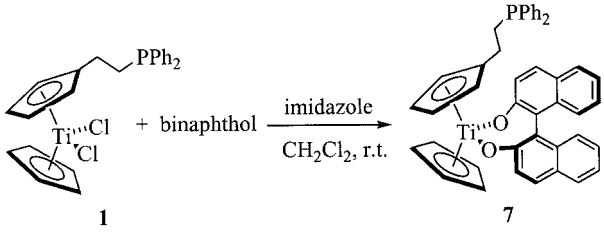
These results prompted us to use the same strategy to convert the titanocene dichloride phosphanes **1** and **2** into optically active ligands. According to well-known procedures for the resolution of titanium metallocenes,[14–18] we carried out the reaction of one equivalent of sodium bi-

[a] Laboratoire de Synthèse et Electrosynthèse Organométalliques, LSEO-UMR 5188, Université de Bourgogne
Faculté des Sciences Gabriel, 6 bd Gabriel, 21000 Dijon, France
Fax: +33-3-8039-6880
E-mail: pierre.le-gendre@u-bourgogne.fr



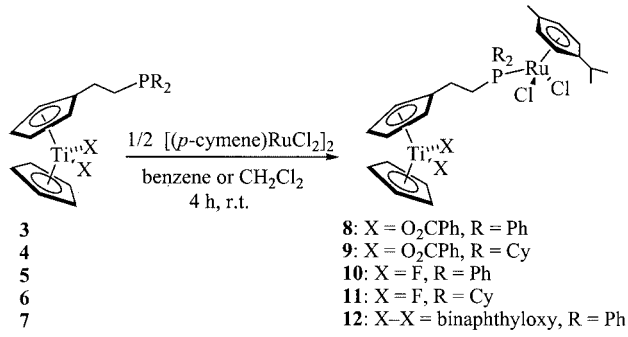
Scheme 1.

naphtholate with **1** in THF at room temperature to afford the desired titanocene binaphtholate phosphane **7**. However, a careful study of the ^{1}H NMR spectrum of the crude product revealed that a partial loss of the $Cp(CH_2)_2PPh_2$ moiety occurs in this reaction. At this step, purification by chromatography is effective but led to a dramatic loss of yield. Therefore we conducted this reaction under milder conditions and used binaphthol directly along with imidazole as an HCl trap (Scheme 2). The reaction proceeded cleanly without any side product formation and in very good yield. The ^{1}H NMR spectrum of **7** differs from that of the precursor phosphane **1** in that it displays four signals for the substituted Cp instead of two. This anisochrony is indicative of a loss of symmetry due to the introduction of binaphthol. The $^{31}P\{^1H\}$ NMR spectrum of **7** displays a single peak at δ = –14.3 ppm, which is shifted slightly downfield with respect to **1**. Thus, starting from a readily commercially available chiral diol, a pure optically active phosphane is available without the usual difficulties of chiral ligand synthesis (resolution, measurement of optical purity, etc.). Finally, it is worth mentioning that all attempts to convert **2** into an optically active phosphane by either the sodium binaphtholate or imidazole routes were unsuccessful.



Scheme 2.

Once this series of new titanocene phosphanes had been prepared, we investigated their complexation with ruthenium by following the procedure previously described for the titanocene dichloride phosphanes **1** and **2**.[5,6] Thus, the treatment of **3**–**6** with 0.5 molar equivalents of the binuclear complex $[(p\text{-cymene})RuCl_2]_2$ in benzene gave the targeted early–late bimetallic complexes **8**–**11**, respectively, in good yields (Scheme 3). The ^{31}P NMR chemical shifts of these complexes, in the δ = 20 ppm range, correspond to a downfield shift of 30–40 ppm relative to the free ligands. As expected, the two carboxylate stretching bands in the IR spectra of **8** and **9** are similar to those reported for the free titanocene phosphanes. The $^{19}F\{^1H\}$ NMR chemical shifts of **10** and **11** show signals in the range of $[Cp_2TiF_2]$ at δ = 62.3 and 62.5 ppm, respectively. This suggests that the dicyclohexylphosphane group is responsible for the deshielding of the signal in the $^{19}F\{^1H\}$NMR spectrum of **6**. All other spectroscopic data of the bimetallic complexes **8**–**11** are in accordance with their structural features.



Scheme 3.

We then carried out the reaction of the optically active phosphane **7** with 0.5 molar equivalents of the binuclear complex $[(p\text{-cymene})RuCl_2]_2$ in CH_2Cl_2. Purification of the crude product by flash chromatography on silica, in order to remove an excess of $[(p\text{-cymene})RuCl_2]_2$, allowed the isolation of the first chiral Ti–Ru bimetallic complex **12**. The $^{31}P\{^1H\}$ NMR spectrum of **12** shows a single peak at δ = 24.7 ppm, which is shifted downfield with respect to **7**. The ^{1}H NMR spectrum of **12** exhibits a marked anisochrony not only for the substituted Cp, as for **7**, but also for the *p*-cymene fragment on the ruthenium centre − a chemical shift gap of 0.25 ppm between both methyl protons of the isopropyl group is observed. At this point, we should mention that the synthesis and the characterisation of chiral early–late bimetallic complexes are remarkably scarce in the literature.[19,20]

Crystals of **8** suitable for X-ray measurements were obtained by slow diffusion of pentane into a saturated dichloromethane solution of the complex. The asymmetric unit contains the bimetallic complex, one dichloromethane solvate and one benzoic acid molecule (originally present as an impurity in the sample). The structure of the complex consists of two fragments: a titanocene moiety with a tetrahedral geometry and a ruthenium moiety with a usual three-legged piano stool structure (Figure 1).[21,22] These two blocks are tethered together through a phosphanylethylene bridge. Most of the structural features of the titanocene dibenzoate fragment within the bimetallic complex **8** are similar to those reported for $[Cp_2Ti(O_2CPh)_2]$,[9,10] as the lengths of the C–O bonds to the coordinated and uncoordinated oxygen atoms are significantly different, the angles at the coordinated oxygen atoms (Ti–O–C) are large and both benzoate ligands tilt with respect to the O(1)–Ti–O(2) plane, with dihedral angles of 42.6(2)° and 29.9(2)°, respectively. Despite the fact that benzoate ligands are rather bulkier than chloride atoms, the phosphorus atom

remains located on the open side of the titanocene but not exactly in the bisecting plane. This asymmetry is induced by a π-stacking effect observed between one phenyl ring of a benzoate ligand and one phenyl ring of a diphenylphosphanyl group. Finally, the cocrystallised benzoic acid molecule forms a hydrogen bond with the oxygen atom O(2) of one benzoate ligand.

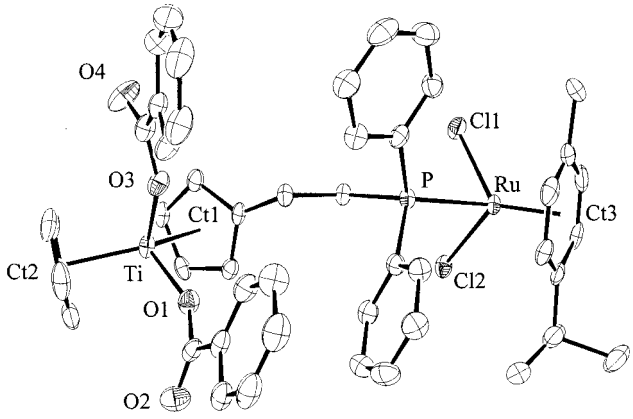


Figure 1. Molecular structure of complex **8**. The CH_2Cl_2 solvate molecule and the benzoic acid have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ti–Ct1 2.049(3), Ti–Ct2 2.054(4), Ti–O1 1.947(2), Ti–O3 1.956(2), Ru–Ct3 1.707(3), Ru–P 2.3516(8), Ru–Cl1 2.4182(9), Ru–Cl2 2.4211(8); Ct1–Ti–Ct2 132.4(2), O1–Ti–O3 90.8(1), Ct3–Ru–P 130.6(1), Ct3–Ru–Cl1 127.3(1), Ct3–Ru–Cl2 124.7(1), P–Ru–Cl1 85.25(3), P–Ru–Cl2 85.89(3), Cl(1)–Ru–Cl(2), 89.16(3) Ti–O(1)–C(35) 152.9(2), Ti–O3–C42 142.4(2).

Crystals of **10** suitable for an X-ray study were also obtained by layering techniques with $CDCl_3$/hexane (the sample came from a NMR solution). The asymmetric unit contains two independent complexes of **10** and six $CDCl_3$ solvate molecules. The two molecules exhibit an almost identical conformation with opposite orientations of the *p*-cymene ligand. The molecular structure of complex **10**, represented in Figure 2, is very similar to the one with two chlorides.[5] The diphenylphosphanyl group is on the open side of the titanocene, near a bisecting position, with both phenyls rings directed toward the titanium atom and the ruthenium away from it in the least congested environment. As expected, the Ti–F bond lengths [<Ti–F> = 1.91(2) Å, mean over four distances] are shorter than the Ti–Cl bond lengths [2.35(3) Å] and the F–Ti–F angle [95(1)°, mean over two angles] similar to the one with chlorides [Cl–Ti–Cl = 95.26(8)°]. These structural parameters are close to those observed for other titanocene difluoride derivatives.[23,24]

Recrystallisation attempts of **12**, starting from a racemic mixture, proved to be difficult, but finally succeeded by slow evaporation under air of a CH_2Cl_2/pentane solution of the crude product. Its molecular structure is shown in Figure 3. The asymmetric unit contains the bimetallic Ti–Ru compound, one additional binaphthol molecule and 2.5 dichloromethane solvates. Contrary to the bimetallic complexes **8** and **10**, the PPh_2 substituent is rotated from the bisecting position, leading to a dihedral angle between the Ct(1)–Ti–Ct(2) plane and the Ct(1)–C(11)–Ct(2) one [C(11) being the

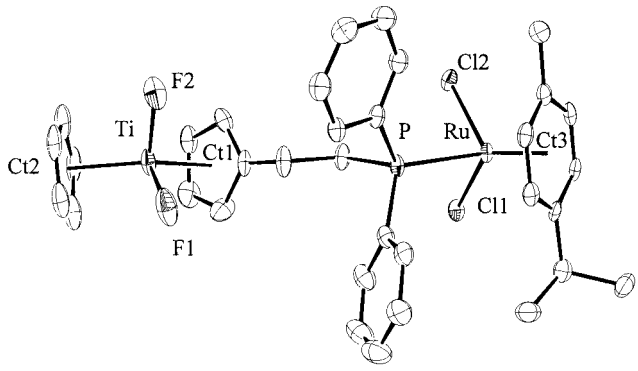


Figure 2. Molecular structure of complex **10**. The $CDCl_3$ solvate molecules have been omitted for clarity. Selected bond lengths [Å] and angles [°] [data in square brackets correspond to the second indepedent molecule]: Ti–Ct1 2.050(5) [2.055(5)], Ti–Ct2 2.065(5) [2.056(5)], Ti–F1 1.891(3) [1.905(4)], Ti–F2 1.937(3) [1.896(4)], Ru–Ct3 1.707(4) [1.709(4)], Ru–P 2.347(1) [2.344(1)], Ru–Cl1 2.4180(12) [2.4093(13)], Ru–Cl2 2.4126(13) [2.4200(11)]; Ct1–Ti–Ct2 132.6(2) [136.2(2)], F1–Ti–F2 93.70(14) [95.7(2)], Ct3–Ru–P 131.0(1) [130.6(1)], Ct3–Ru–Cl1 126.1(1) [126.1(1)], Ct3–Ru–Cl2 127.7(1) [127.3(1)], P–Ru–Cl1 84.35(3) [83.47(3)], P–Ru–Cl2 86.92(4) [86.74(4)], Cl1–Ru–Cl2 86.80(4) [86.84(4)].

methylene carbon atom attached to the Cp ring] of 67°. Thus, the areneruthenium moiety lies in an open area and not above the bulky binaphtholate group. The structural parameters of the chelate ring formed are similar to those described in the literature.[14–17] The bite angle O(1)–Ti–O(2) is equal to 92.0(1)° and the dihedral angle between the naphthalene planes [64.8(1)°] is contracted from that of cocrystallised "free" binaphthol (90° is generally observed). It is noteworthy that two different Ti–O bond lengths are observed [Ti–O(1) = 1.915(2) Å and Ti–O(2) = 1.981(2) Å]. This can be explained by the presence of a hydrogen bond pointing from a hydroxide group of the "free" binaphthol molecule toward the O(2) atom [O(3)–H···O(2) = 1.75 Å]. In fact, this binaphthol molecule plays an active role in the crystallisation process in connecting two adjacent molecules: the second hydroxy group points between the two chlorine atoms of the Ru moiety of an adjacent complex [O(4)–H···Cl(1) = 2.35 Å and O(4)–H···Cl(2) = 2.70 Å].[25]

Conclusions

This study provides a straightforward access to a series of new early–late transition metal complexes. The substitution of both chloride atoms of a titanocene phosphane by other ligands such as benzoate, fluoride or binaphtholate is the key step of this new route. The phosphanes so formed react readily with the binuclear complex [(*p*-cymene)-$RuCl_2$]$_2$ to give the targeted bimetallic complexes. The structures of three of them have been confirmed by X-ray diffraction studies. Assessment of the catalytic behaviour of these early–late bimetallic complexes is currently being studied in our laboratory. The design of new titanocene phosphanes inspired by the fruitful chemistry of $[Cp_2TiCl_2]$ is also in progress.

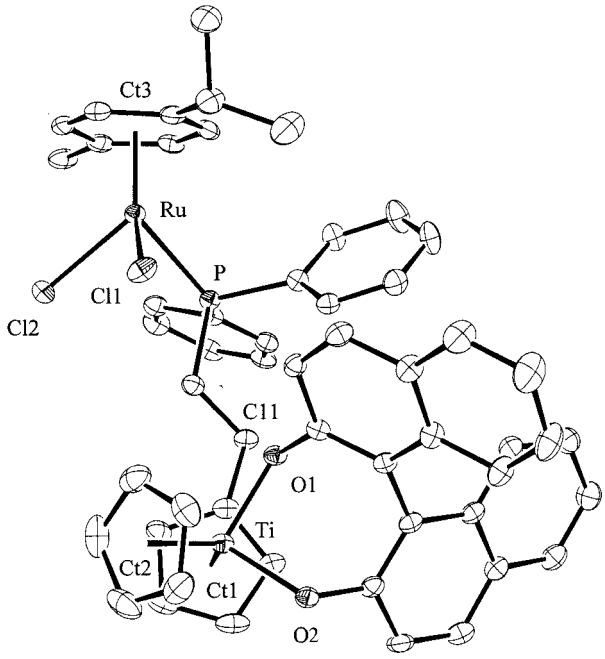


Figure 3. Molecular structure of complex *rac*-**12**. Only one enantiomer is shown for clarity. The free binaphthol molecule and the CH_2Cl_2 solvate molecules are also not shown. Selected bond lengths [Å] and angles [°]: Ti–Ct1 2.099(3), Ti–Ct2 2.088(4), Ti–O1 1.915(2), Ti–O2 1.981(2), Ru–Ct3 1.703(3), Ru–P 2.3442(8), Ru–Cl1 2.4210(7), Ru–Cl2 2.4157(8); Ct1–Ti–Ct2 130.48(13), O1–Ti–O2 91.96(9), Ct3–Ru–P 130.95(9), Ct3–Ru–Cl1 126.04(9), Ct3–Ru–Cl2 126.42(9), P–Ru–Cl1 84.97(3), P–Ru–Cl2 86.80(3), Cl1–Ru–Cl2 87.22(3).

Experimental Section

General Remarks: All reactions were carried out under an atmosphere of purified argon. The solvents and eluents were dried by the appropriate procedures and distilled under argon immediately before use. Standard Schlenk techniques and conventional glass vessels were employed. Elemental analyses were carried out with a EA 1108 CHNS-O FISONS Instruments. ^{1}H (500 MHz), ^{19}F (282 MHz) and ^{31}P{^{1}H} (202 MHz) spectra were collected on a Bruker 500 MHz Avance DRX spectrometer. Chemical shifts are quoted relative to internal TMS (^{1}H), external $CFCl_3$ (^{19}F) or external H_3PO_4 (^{31}P). IR spectra were obtained with a Bruker IFS 66v spectrometer. The titanocene phosphanes **1** and **2** were synthesised as reported previously.[5,6]

[Ti(O$_2$CPh)$_2$(η^5-C$_5$H$_5$){η^5-C$_5$H$_4$(CH$_2$)$_2$PPh$_2$}] (3): A 100-mL flask was charged with $PhCO_2Na$ (0.3 g, 2 mmol), [$TiCl_2$(η^5-C_5H_5){η^5-$C_5H_4(CH_2)_2PPh_2$}] (**1**; 0.4 g, 1 mmol), 5 mL of degassed water and 44 mL of $CHCl_3$. The mixture was stirred for 1.5 h during which time the colour turned to orange. Then, the organic phase was removed, washed with 5 mL of water, dried with $MgSO_4$, filtered and the solvents evaporated to dryness to yield an orange powder (0.45 g, 75% yield). IR (KBr): ν(COO) = 1634, 1324 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 2.17 (t, $^3J_{H,H}$ = 8 Hz, 2 H, CH_2), 2.61 (pseudo q, $^3J_{H,H}$ = $^2J_{H,P}$ = 8 Hz, 2 H, CH_2), 6.42 (pseudo t, $^3J_{H,H}$ = $^4J_{H,H}$ = 3 Hz, 2 H, C_5H_4), 6.59 (s, 5 H, C_5H_5), 6.61 (pseudo t, $^3J_{H,H}$ = $^4J_{H,H}$ = 3 Hz, 2 H, C_5H_4), 7.16–7.20 (m, 10 H, PPh_2), 7.44 (pseudo t, $^3J_{H,H}$ = 7 Hz, 4 H, Ph), 7.54 (t, $^3J_{H,H}$ = 7 Hz, 2 H, Ph), 8.03 (d, $^3J_{H,H}$ = 7 Hz, 4 H, Ph) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = –14.87 (s, PPh_2) ppm. $C_{38}H_{33}O_4PTi$ (632.51): calcd. C 72.16, H 5.26; found C 72.00, H 5.02.

[Ti(O$_2$CPh)$_2$(η^5-C$_5$H$_5$){η^5-C$_5$H$_4$(CH$_2$)$_2$PCy$_2$}] (4): This compound was obtained following the above procedure but with [$TiCl_2$(η^5-C_5H_5){η^5-$C_5H_4(CH_2)_2PCy_2$}] (**2**) and toluene/H_2O as the biphasic system (0.38 g, 62% yield). IR (KBr): ν(COO) = 1635, 1326 cm^{-1}. ^{1}H NMR (C_6D_6): δ = 1.10–1.90 (m, 24 H, Cy + CH_2), 2.85 (pseudo q, $^3J_{H,H}$ = $^2J_{H,P}$ = 8 Hz, 2 H, CH_2), 6.14 (pseudo t, $^3J_{H,H}$ = $^4J_{H,H}$ = 3 Hz, 2 H, C_5H_4), 6.28 (s, 5 H, C_5H_5), 6.41 (pseudo t, $^3J_{H,H}$ = $^4J_{H,H}$ = 3 Hz, 2 H, C_5H_4), 7.35 (t, $^3J_{H,H}$ = 8 Hz, 2 H, Ph), 7.39 (pseudo t, $^3J_{H,H}$ = 8 Hz, 4 H, Ph), 8.54 (d, $^3J_{H,H}$ = 8 Hz, 4 H, Ph) ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ = –3.79 (s, PCy_2) ppm. $C_{38}H_{45}O_4PTi$ (644.60): calcd. C 70.80, H 7.04; found C 70.54, H 7.16.

[TiF$_2$(η^5-C$_5$H$_5$){η^5-C$_5$H$_4$(CH$_2$)$_2$PPh$_2$}] (5): A 100-mL flask was charged with NaF (0.065 g, 1.54 mmol), [$TiCl_2$(η^5-C_5H_5){η^5-$C_5H_4(CH_2)_2PPh_2$}] (**1**; 0.36 g, 0.78 mmol), 4 mL of degassed water and 36 mL of $CHCl_3$. The mixture was stirred for 1.5 h during which time the colour turned to deep yellow. Then, the organic phase was removed, washed with 5 mL of water, dried with $MgSO_4$, filtered and the solvents evaporated to dryness to yield a yellow powder (0.16 g, 50% yield). ^{1}H NMR ($CDCl_3$): δ = 2.29 (t, $^3J_{H,H}$ = 8 Hz, 2 H, CH_2), 2.65 (pseudo q, $^3J_{H,H}$ = $^2J_{H,P}$ = 8 Hz, 2 H, CH_2), 6.05 (pseudo s, 2 H, C_5H_4), 6.38 (m, 7 H, C_5H_5 + 2 H C_5H_4), 7.25–7.35 (m, 6 H, PPh_2), 7.37–7.44 (m, 4 H, PPh_2) ppm. ^{19}F NMR ($CDCl_3$): δ = 64.28 (s, TiF_2) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = –14.99 (s, PPh_2) ppm. $C_{24}H_{23}F_2PTi$ (428.28): calcd. C 67.31, H 5.41; found C 66.82, H 5.26.

[TiF$_2$(η^5-C$_5$H$_5$){η^5-C$_5$H$_4$(CH$_2$)$_2$PCy$_2$}] (6): This compound was obtained following the above procedure but with [$TiCl_2$(η^5-C_5H_5){η^5-$C_5H_4(CH_2)_2PCy_2$}] (**2**) and toluene/H_2O as the biphasic system (0.17 g, 50% yield). ^{1}H NMR (C_6D_6): δ = 1.10–1.27 (m, 12 H, Cy), 1.55–1.84 (m, 12 H, Cy+CH_2), 2.87 (pseudo q, $^3J_{H,H}$ = $^2J_{H,P}$ = 8 Hz, 2 H, CH_2), 5.84 (pseudo s, 4 H, C_5H_4), 5.99 (s, 5 H, C_5H_5) ppm. ^{19}F NMR (C_6D_6): δ = 86.76 (s, TiF_2) ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ = –3.41 (s, PCy_2) ppm. $C_{24}H_{35}F_2PTi$ (440.37): calcd. C 65.46, H 8.01; found C 65.15, H 8.22.

[Ti{(*R*)-Binaphtholate)}(η^5-C$_5$H$_5$){η^5-C$_5$H$_4$(CH$_2$)$_2$PPh$_2$}] (7): Imidazole (0.14 g, 2.15 mmol) in 10 mL of dichloromethane and (*R*)-binaphthol (0.32 g, 1.13 mmol) in 25 mL of dichloromethane were successively added to a solution of [$TiCl_2$(η^5-C_5H_5){η^5-C_5H_4-$(CH_2)_2PPh_2$}] (**1**; 0.52 g, 1.13 mmol) in 25 mL of dichloromethane at room temperature. The mixture was stirred for 4 h. After filtration, the solvent was removed from the filtrate under reduced pressure and 40 mL of toluene was added to the resulting product. Filtration through celite and evaporation of the solvent afforded **7** (0.5 g, 70% yield) as a red solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.65–1.75 (m, 2 H, CH_2), 2.20–2.35 (m, 2 H, CH_2), 5.28–5.35 (m, 1 H, C_5H_4), 5.85–5.95 (m, 1 H, C_5H_4), 5.98–6.04 (m, 1 H, C_5H_4), 6.09 (s, 5 H, C_5H_5), 6.60–6.66 (m, 1 H, C_5H_4), 7.15–8.15 (m, 22 H, phenyl-*H* and binaphthyl-*H*) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz): δ = –14.3 (s, PPh_2) ppm. $C_{44}H_{35}PTiO_2$ (674.59): calcd. C 78.34, H 5.23; found C 78.48, H 5.29. $[\alpha]_D^{20}$ = –2163 (*c* = 0.1, CH_2Cl_2).

[(*p*-Cymene)RuCl$_2$}{(η^5-C$_5$H$_5$)[μ-η^5:η^1-C$_5$H$_4$(CH$_2$)$_2$PPh$_2$[Ti(O$_2$CPh)$_2$}] (8): A 25-mL Schlenk flask was charged under argon with **3** (0.45 g, 0.71 mmol), [(*p*-cymene)$RuCl_2$]$_2$ (0.16 g, 0.27 mmol) and degassed benzene. The mixture was stirred at room temperature for 4 h, during which time a brick-red precipitate slowly formed. The solvent was removed by filtration and the red residue was dried under vacuum (0.38 g, 75% yield). IR (KBr): ν(COO) = 1636, 1355 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.74 [d, $^3J_{H,H}$ = 7 Hz, 6 H, CH-

(CH_3)$_2$], 1.81 (s, 3 H, CH_3), 2.17 (m, 2 H, CH_2), 2.45 [sept, $^3J_{H,H}$ = 7 Hz, 1 H, CH(CH$_3$)$_2$], 2.63 (m, 2 H, CH_2), 5.01 (d, $^3J_{H,H}$ = 6 Hz, 2 H, *p*-cymene), 5.18 (d, $^3J_{H,H}$ = 6 Hz, 2 H, *p*-cymene), 6.14 (pseudo t, $^3J_{H,H}$ = $^4J_{H,H}$ = 2 Hz, 2 H, C$_5H_4$), 6.48 (pseudo t, $^3J_{H,H}$ = $^4J_{H,H}$ = 2 Hz, 2 H, C$_5H_4$), 6.49 (s, 5 H, C$_5H_5$), 7.19 (pseudo t, $^3J_{H,H}$ = 6 Hz, 4 H, PPh$_2$), 7.25–7.35 (m, 6 H, PPh$_2$), 7.49 (t, $^3J_{H,H}$ = 8 Hz, 2 H, Ph), 7.56 (pseudo t, $^3J_{H,H}$ = 8 Hz, 4 H, Ph), 7.82 (d, $^3J_{H,H}$ = 8 Hz, 4 H, Ph) ppm. ^{31}P{^{1}H} NMR (202 MHz, CDCl$_3$): δ = 24.99 (s, PPh$_2$) ppm. $C_{48}H_{47}Cl_2O_4PRuTi$ (938.70): calcd. C 61.42, H 5.05; found C 60.92, H 5.21.

[(*p*-Cymene)RuCl$_2$\{(η^5-C$_5$H$_5$)[μ-η^5:η^1-C$_5$H$_4$(CH$_2$)$_2$PCy$_2$]Ti(O$_2$CPh)$_2$\}] (9): This compound was obtained following the above procedure but with **4** (0.41 g, 80% yield). IR (KBr): ν(COO) = 1635, 1328 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 0.85–2.17 (m, 24 H, Cy + CH_2), δ = 1.24 [d, $^3J_{H,H}$ = 7 Hz, 6 H, CH(CH_3)$_2$], 2.02 (s, 3 H, CH_3), 2.60 (m, 2 H, CH_2), 2.75 [sept, $^3J_{H,H}$ = 7 Hz, 1 H, CH(CH$_3$)$_2$], 5.01 (pseudo s,, 4 H, *p*-cymene), 6.37 (pseudo t, $^3J_{H,H}$ = $^4J_{H,H}$ = 3 Hz, 2 H, C$_5H_4$), 6.55 (pseudo t, $^3J_{H,H}$ = $^4J_{H,H}$ = 3 Hz, 2 H, C$_5H_4$), 6.60 (s, 5 H, C$_5H_5$), 7.46 (pseudo t, $^3J_{H,H}$ = 8 Hz, 4 H, Ph), 7.50 (t, $^3J_{H,H}$ = 8 Hz, 2 H, Ph), 8.07 (d, $^3J_{H,H}$ = 8 Hz, 4 H, Ph) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 25.84 (s, PCy$_2$) ppm. $C_{48}H_{59}Cl_2O_4PRuTi$ (950.80): calcd. C 60.23, H 6.25; found C 60.43, H 6.55.

[(*p*-Cymene)RuCl$_2$\{(η^5-C$_5$H$_5$)[μ-η^5:η^1-C$_5$H$_4$(CH$_2$)$_2$PPh$_2$]TiF$_2$\}] (10): This compound was obtained following the procedure described for the synthesis of **8** but with **5** (0.33 g, 83% yield). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 0.80 [d, $^3J_{H,H}$ = 7 Hz, 6 H, CH(CH_3)$_2$], 1.90 (s, 3 H, CH_3), 2.25 (m, 2 H, CH_2), 2.52 [sept, $^3J_{H,H}$ = 7 Hz, 1 H, CH(CH$_3$)$_2$], 2.74 (m, 2 H, CH_2), 5.09 (d, $^3J_{H,H}$ = 8 Hz, 2 H, *p*-cymene), 5.28 (d, $^3J_{H,H}$ = 8 Hz, 2 H, *p*-cymene), 5.93 (pseudo s, 2 H, C$_5H_4$), 6.25 (pseudo s, 2 H, C$_5H_4$), 6.36 (s, 5 H, C$_5H_5$), 7.48 (m, 6 H, PPh$_2$), 7.90 (m, 4 H, PPh$_2$) ppm. ^{19}F NMR (CDCl$_3$): δ = 62.29 (s, TiF_2) ppm. ^{31}P{^{1}H} NMR (202 MHz, CDCl$_3$): δ = 24.57 (s, PPh$_2$) ppm. $C_{34}H_{37}Cl_2F_2PRuTi$ (734.47): calcd. C 55.60, H 5.08; found C 55.10, H 4.90.

[(*p*-Cymene)RuCl$_2$\{(η^5-C$_5$H$_5$)[μ-η^5:η^1-C$_5$H$_4$(CH$_2$)$_2$PCy$_2$]TiF$_2$\}] (11): This compound was obtained following the procedure described for the synthesis of **8** but with **6** (0.24 g, 60% yield). ^{1}H NMR (CDCl$_3$): δ = 1.10–2.31 (m, 24 H, Cy + CH_2), δ = 1.24 [d, $^3J_{H,H}$ = 7 Hz, 6 H, CH(CH_3)$_2$], 2.11 (s, 3 H, CH_3), 2.65 (m, 2 H, CH_2), 2.85 [sept, $^3J_{H,H}$ = 7 Hz, 1 H, CH(CH$_3$)$_2$], 5.58 (pseudo s, 4 H, *p*-cymene), 6.14 (pseudo t, $^3J_{H,H}$ = $^4J_{H,H}$ = 3 Hz, 2 H, C$_5H_4$), 6.31 (pseudo t, $^3J_{H,H}$ = $^4J_{H,H}$ = 3 Hz, 2 H, C$_5H_4$), 6.42 (s, 5 H, C$_5H_5$) ppm. ^{19}F NMR (CDCl$_3$): δ = 62.54 (s, TiF_2) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 25.88 (s, PCy$_2$) ppm. $C_{34}H_{49}Cl_2F_2PRuTi$ (746.57): calcd. C 54.70, H 6.61; found C 54.55, H 6.41.

[(*p*-Cymene)RuCl$_2$\{(η^5-C$_5$H$_5$)[μ-η^5:η^1-C$_5$H$_4$(CH$_2$)$_2$PPh$_2$]Ti[(*R*)-binaphtholate)]\}] (12): [(*p*-cymene)RuCl$_2$]$_2$ (0.041 g, 0.07 mmol) in 5 mL of dichloromethane was added to a solution of **7** (0.1 g, 0.15 mmol) in 10 mL of dichloromethane at 0 °C. The mixture was stirred at room temperature for 4 h. The solvent was then removed in vacuo. Purification by flash chromatography on silica (toluene/THF, 50:50) under argon and at 10 °C afforded **12** as an orange solid (0.070 g, 50% yield). Complex **12** in its racemic form, which was used to obtain suitable crystal for X-ray diffraction, was prepared in a similar way. ^{1}H NMR (CDCl$_3$, 500 MHz): δ = 0.70 [d, $^3J_{H,H}$ = 7 Hz, 3 H, CH(CH_3)$_2$], 0.95 [d, $^3J_{H,H}$ = 7 Hz, 3 H, CH(CH_3)$_2$], 1.67–1.80 (m, 1 H, CH_2), 1.87 (s, 3 H, CH_3), 2.00–2.19 (m, 1 H, CH_2), 2.45–2.65 (m, 1 H, CH_2), 2.54 [sept, $^3J_{H,H}$ = 7 Hz, 1 H, CH(CH$_3$)$_2$], 2.74–2.96 (m, 1 H, CH$_2$), 4.76–4.81 (m, 1 H, C$_5H_4$), 4.88 (d, $^3J_{H,H}$ = 6 Hz, 1 H, *p*-cymene), 5.19 (d, $^3J_{H,H}$ = 6 Hz, 1 H, *p*-cymene), 5.28 (d, $^3J_{H,H}$ = 6 Hz, 1 H, *p*-cymene), 5.39 (d, $^3J_{H,H}$ = 6 Hz, 1 H, *p*-cymene), 5.97–6.04 (m, 1 H, C$_5H_4$), 6.09–6.15 (m, 1 H, C$_5H_4$), 6.20 (s, 5 H, C$_5H_5$), 6.49–6.57 (m, 1 H, C$_5H_4$), 6.80–8.00 (m, 22 H, Ph and binaphthyl) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$, 202 MHz): δ = 24.66 (s) ppm. $C_{54}H_{49}Cl_2O_2PRuTi$ (980.78): calcd. C 66.13, H 5.04; found C 66.60, H 5.10. $[\alpha]_D^{20}$ = –1920 (*c* = 0.1, CH_2Cl_2).

X-ray Crystallographic Study of 8: $C_{48}H_{47}Cl_2O_4PRuTi\cdot C_7H_6O_2\cdot 0.5(CH_2Cl_2)$, *MW* = 1103.28, monoclinic, space group *C*2/*c*, *a* = 25.0136(3), *b* = 18.9231(2), *c* = 21.2279(3) Å, β = 98.595(1)°, *V* = 9935.1 (2) Å^3, *Z* = 8, D_{calc} = 1.475 g cm^{-3}; *F*(000) = 4536. The structure was solved by the heavy-atom method using SHELXS97.[26] Refinement, based on F^2, was carried out by full-matrix least-squares with the SHELXL97 and WINGX programs.[26,27] Non-hydrogen atoms were refined anisotropically. H atoms were included in calculated positions and included in the refinement with a riding-motion model with U_{iso} = 1.2U_{eq} of the carrier atom (1.5 for methyl groups and OH). Convergence was reached at wR_2 = 0.125 for all data (11386 intensities), R_1 = 0.047 for 7904 intensities with $I > 2\sigma(I)$ and *S* = 1.044 for 615 parameters. The residual electron density in the final difference Fourier map was 1.12 and –1.18 e Å^{-3}.

X-ray Crystallographic Study of 10: $C_{34}H_{37}Cl_2F_2PRuTi\cdot 3(CHCl_3)$, *MW* = 1092.6, triclinic, space group $P\bar{1}$; *a* = 9.716(5), *b* = 17.008(5), *c* = 28.927(5) Å, α = 75.609(5)°, β = 82.660(5)°, γ = 81.094(5)°, *V* = 4554 (3) Å^3, *Z* = 4, D_{calc} = 1.593 g cm^{-3}; *F*(000) = 2192. The structure was solved by the heavy-atom method using SHELXS97.[26] Refinement, based on F^2, was carried out by full-matrix least-squares with the SHELXL97 and WINGX programs.[26,27] Non-hydrogen atoms were refined anisotropically. H atoms were included in calculated positions and included in the refinement with a riding-motion model with U_{iso} = 1.2U_{eq} of the carrier atom (1.5 for methyl groups). Two independent molecules of **10** are present in the asymmetric unit and one of them has a disordered cyclopentadienyl ring over two positions with occupancies refined to 0.53:0.47. Among the six chloroform solvates present in the asymmetric unit, three are disordered over two positions with occupancies refined to 0.59:0.41, 0.90:0.10 and 0.90:0.10. The chlorine atoms with occupancies equal to 0.10 were isotropically refined Convergence was reached at wR_2 = 0.119 for all data (18928 intensities), R_1 = 0.051 for 15240 intensities with $I > 2\sigma(I)$ and *S* = 1.039 for 1047 parameters. The residual electron density in the final difference Fourier map was 1.25 and –1.03 e Å^{-3}.

X-ray Crystallographic Study of 12: $C_{54}H_{49}Cl_2O_2PRuTi\cdot C_{20}H_{14}O_2\cdot 2.5(CH_2Cl_2)$, *MW* = 1479.4, triclinic, space group $P\bar{1}$; *a* = 12.8350(4), *b* = 15.5480(5), *c* = 19.4240(6) Å, α = 112.361(2)°, β = 97.889(2)°, γ = 105.773(2)°, *V* = 3321.2 (2) Å^3, *Z* = 2, D_{calc} = 1.479 g cm^{-3}; *F*(000) = 1518. The structure was solved by the heavy-atom method using SHELXS97.[26] Refinement, based on F^2, was carried out by full-matrix least-squares with the SHELXL97 and WINGX programs.[26,27] Non-hydrogen atoms were refined anisotropically. H atoms were included in calculated positions and included in the refinement with a riding-motion model with U_{iso} = 1.3U_{eq} of the carrier atom. Two of the three dichloromethane solvates are disordered: one, located close to an inversion centre, was refined with an occupation factor of 0.5, the other is disordered over two positions with occupancies refined to 0.77:0.23. Convergence was reached at wR_2 = 0.129 for all data, R_1 = 0.049 for 12707 intensities with $I > 2\sigma(I)$ and *S* = 1.053 for 841 parameters. The residual electron density in the final difference Fourier map was 1.8 and –1.7 e Å^{-3} close to a disordered dichloromethane solvate.

CCDC-256921 (for **8**), -256922 (for **10**) and -225303 (for **12**) contain the supplementary crystallographic data for this paper. These

data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[1] R. Choukroun, D. Gervais, P. Kalck, F. Senocq, *J. Organomet. Chem.* **1987**, *335*, C9–C12.
[2] A. M. Trzeciak, J. J. Ziolkowski, R. Choukroun, *J. Mol. Catal.* **1996**, *110*, 135–139.
[3] B. E. Bosch, I. Brümmer, K. Kunz, G. Erker, R. Fröhlich, S. Kotila, *Organometallics* **2000**, *19*, 1255–1261.
[4] N. Wheatley, P. Kalck, *Chem. Rev.* **1999**, *99*, 3379–3419.
[5] P. Le Gendre, P. Richard, C. Moïse, *J. Organomet. Chem.* **2000**, *605*, 151–156.
[6] P. Le Gendre, M. Picquet, P. Richard, C. Moïse, *J. Organomet. Chem.* **2002**, *643–644*, 231–236.
[7] P. Le Gendre, V. Comte, A. Michelot, C. Moïse, *Inorg. Chim. Acta* **2003**, *350*, 289–292.
[8] J. Goux, P. Le Gendre, P. Richard, C. Moïse, *J. Organomet. Chem.* **2004**, in press.
[9] K. Döppert, H. P. Klein, U. Thewalt, *J. Organomet. Chem.* **1986**, *303*, 205–211.
[10] D. M. Hoffman, N. D. Chester, R. C. Fay, *Organometallics* **1983**, *2*, 48–52.
[11] A. Herzog, F. Q. Liu, H. W. Roesky, A. Demsar, K. Keller, M. Noltemeyer, F. Pauer, *Organometallics* **1994**, *13*, 1251–1256.
[12] X. Verdaguer, M. C. Hansen, S. C. Berk, S. L. Buchwald, *J. Org. Chem.* **1997**, *62*, 8522–8528.
[13] F. Lunzer, C. Marschner, S. Landgraf, *J. Organomet. Chem.* **1998**, *568*, 253–255.
[14] F. R. W. P. Wild, L. Zsolnai, G. Huttner, H. H. Brintzinger, *J. Organomet. Chem.* **1982**, *232*, 233–247.
[15] M. E. Huttenloch, B. Dorer, U. Rief, M. H. Prosenc, K. Schmidt, H. H. Brintzinger, *J. Organomet. Chem.* **1997**, *541*, 219–232.
[16] M. S. Erickson, F. R. Fronczek, M. L. McLaughlin, *J. Organomet. Chem.* **1991**, *415*, 75–85.
[17] B. A. Kuntz, R. Ramachandran, N. J. Taylor, J. Guan, S. Collins, *J. Organomet. Chem.* **1995**, *497*, 133–142.
[18] S. Collins, B. A. Kuntz, Y. Hong, *J. Org. Chem.* **1989**, *54*, 4154–4158.
[19] A. Kless, C. Lefeber, A. Spannenberg, R. Kempe, W. Baumann, J. Holz, A. Börner, *Tetrahedron* **1996**, *52*, 14599–14606.
[20] M. Quirmbach, A. Kless, J. Holz, V. Tararov, A. Börner, *Tetrahedron: Asymmetry* **1999**, *10*, 1803–1811.
[21] J. F. Mai, Y. Yamamoto, *J. Organomet. Chem.* **1998**, *560*, 223–232.
[22] J. F. Mai, Y. Yamamoto, *J. Organomet. Chem.* **1997**, *545*, 577–579.
[23] C. H. Winter, X. X. Zhou, M. J. Heeg, *Inorg. Chem.* **1992**, *31*, 1808–1815.
[24] A. J. Edwards, N. J. Burke, C. M. Dobson, K. Prout, S. J. Heyes, *J. Am. Chem. Soc.* **1995**, *117*, 4637–4653.
[25] G. Aullon, D. Bellamy, L. Brammer, E. A. Bruton, A. G. Orpen, *Chem. Commun.* **1998**, 653–654.
[26] G. M. Sheldrick, SHELX97 (includes SHELXS97, SHELXL97); Programs for Crystal Structure Analysis (Release 97-2); University of Göttingen, Göttingen, Germany, **1998**.
[27] L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837–838.

Received: December 14, 2004

