ORGANOMETALLICS

Volume 27, Number 9, May 12, 2008

Communications

Synthesis and Reactivity of P-Chiral Tethered (η^1:η^6-phosphinoarene)ruthenium Complexes

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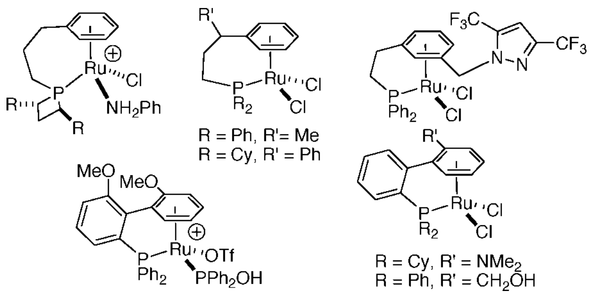
Received January 28, 2008

Summary: A new group of tethered phosphinoarene ruthenium complexes containing a stereogenic center at the phosphine atom is presented. The introduction of other elements of chirality, either as a plane or at the ruthenium center, is explored.

The chemistry of Ru(II) complexes stabilized by phosphorus donor ligands has received considerable attention in recent years, since the discovery of important catalytic systems such as Noyori's BINAP and Grubbs' carbene catalyst.[1,2] A rigid chiral environment around the metal center in transition-metal complexes is an interesting goal when these compounds are used for the discrimination of prochiral substrates in catalytic organic synthesis.[3,4] With this purpose a new family of chiral tethered ruthenium phosphinoarene complexes have been prepared. Recent examples of chiral ruthenium complexes of this type have been described, in which the phosphinoarene chelates have a stereogenic center located in the bridge,[5] planar chirality,[6] or a stereogenic center in the phosphine substituents.[7] Other η^6:η^1-arene complexes containing nitrogen, oxygen, sulfur, or carbene coordination arms are also known[8] (Scheme 1).

Scheme 1



The new complexes are built up on the chiral framework of an enantiopure P-stereogenic phosphine. The starting materials were obtained by the enantioselective deprotonation methodo-

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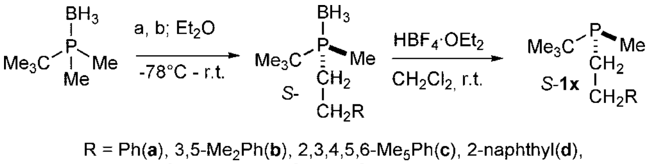
10.1021/om800076x CCC: $40.75

Scheme 2. Preparation of the Phosphines a−f[a]

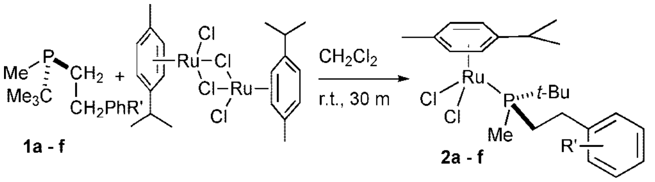


R = Ph(**a**), 3,5-Me$_2$Ph(**b**), 2,3,4,5,6-Me$_5$Ph(**c**), 2-naphthyl(**d**), 3-(OMe)Ph(**e**), 3-(CF$_3$)Ph(**f**)

[a] Legend: (a) *s*-BuLi/(−)-sparteine; (b) XCH$_2$R.

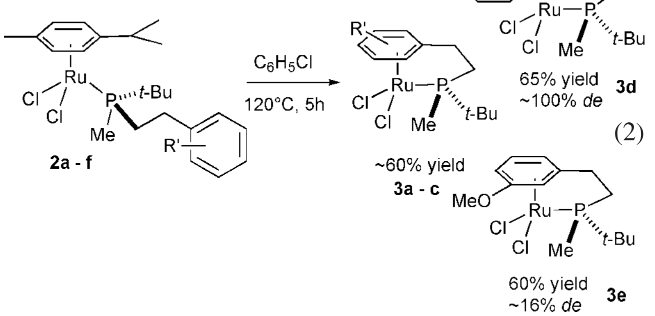
logy proposed by Evans,[9] using sparteine as chiral auxiliary. By this method the first recrystallization of the borane-protected phosphine gave the pure *S* enantiomer with yields between 35 and 68%[10] (Scheme 2).

The ruthenium-tethered complexes were obtained in two successive steps: initial coordination of pure deprotected phosphine over ruthenium arene halide dimers, followed by intramolecular arene substitution (eqs 1 and 2).[11]



R' = H(**a**), 3,5-Me$_2$(**b**), 2,3,4,5,6-Me$_5$(**c**), 2-naphthyl(**d**), 3-OMe(**e**), 3-CF$_3$(**f**)

(1)



(2)

When the phosphine contains nonsymmetric aryl groups as in the case of **2d**,**e**, a stereogenic plane is created in this process. Complete diastereoselectivity was observed in the intramolecular arene substitution for **3d**, but mixtures of both diastereoisomers were obtained in the arene ligand displacement reaction for **3e**.

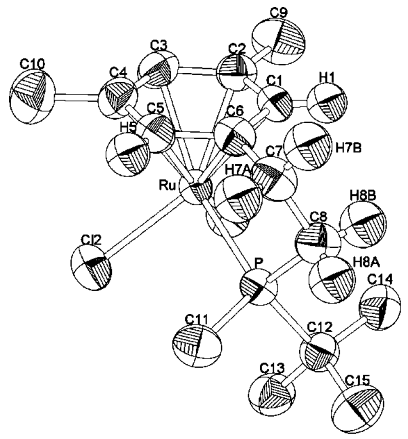


Figure 1. ORTEP drawing of the molecular structure of **3b**, shown at the 50% probability level. Some hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ru−Cl(2), 2.3925(13); Ru−Cl(1), 2.4267(13); Ru−P, 2.3299(10); P−Ru−Cl(2), 88.93(4); P−Ru−Cl(1), 96.95(3); Cl(2)−Ru−Cl(1), 85.61(4); Ru−C(6), 2.165(4); Ru−C(3), 2.244(3); P−C(8)−C(7)−C(6), 43.540.

Decomposition of **2f** was observed when the same intramolecular substitution was carried out under the same conditions, even starting from the dinuclear ruthenium complex [RuCl(μ-Cl)(C$_6$H$_6$)]$_2$. In **3d** the NOE contacts between the three arene protons and the *tert*-butyl or methyl phosphine fragments showed that the terminal phenyl ring of the naphthyl substituent is distal to the *tert*-butyl group.

The proton NMR of **3c** in *d*$_8$-toluene showed the signals of the five different methyl substituents of the arene group. Only the signal of the 4-methyl group appears significantly coupled to the phosphorus atom, as could be confirmed by the ^{1}H{^{31}P} NMR spectrum. When the spectrum was obtained at 220 K, the signal at 1.08 ppm of the *tert*-butyl group collapsed, revealing hindered rotation about the P−CMe$_3$ bond.[12]

The molecular structure of the tethered complex **3b** was determined by single-crystal X-ray analysis (Figure 1).[13] The molecular structure corresponds to a distorted pseudo-octahedral geometry around the ruthenium center. Bond distances and angles are similar to those previously reported for related tethered complexes.[14]

The coplanarity of the benzylic carbon with the mean plane defined by the arene atoms, observed when the bridging P-arene

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(10) Typical procedure for the synthesis of phosphines **a**−**f**: (*S*)-*tert*-butyl(2-phenylethyl)methylphosphine−borane (**a**). (−)-Sparteine (5.53 g, 23.6 mmol) was dissolved in 50 mL of diethyl ether, and the solution was cooled to −78 °C with stirring. A *sec*-butyllithium solution (17.5 mL of 1.3 M solution in hexanes) was added by syringe. After 10 min, a solution of *tert*-butyldimethylphosphine−borane (2.50 g, 18.9 mmol) in diethyl ether (45 mL) was added by syringe and the solution was stirred at −78 °C. Three hours later benzyl bromide (3.40 mL, 28.3 mmol) was added. The reaction mixture was warmed to room temperature overnight and then was quenched by the addition of 50 mL of water. The suspension was extracted with diethyl ether (3 × 40 mL). The combined organic layers were dried with sodium sulfate and filtered, and the solvent was removed in vacuo. The resulting residue was purified by chromatography on silica gel (hexane−ethyl acetate, increasing polarity), furnishing the product (2.80 g, 67%). Optically pure product was obtained by recrystallization from hexane. ^{31}P{^{1}H} NMR (101.2 MHz, C$_6$H$_5$Cl, 298 K; δ (ppm)): 25.0 (q, $J_{PB} \approx 60.0$ Hz). ^{1}H NMR, ^{13}C NMR, IR, and elemental analysis data are given in the Supporting Information.

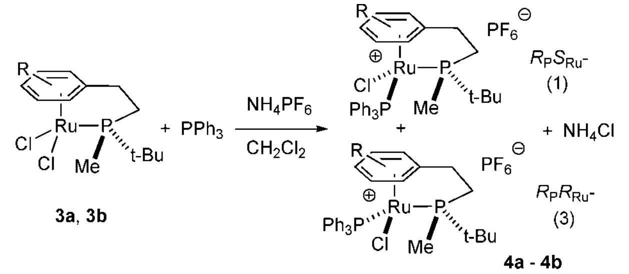
(11) Typical procedure for the synthesis of complexes **2**: dichloro(η^6-*p*-cymene)((*R*)-*tert*-butylmethyl(2-phenylethyl)phosphine)ruthenium(II) (**2a**). A 2.00 mL portion of tetrafluoroboric acid diethyl ether complex (2.38 g, 14.6 mmol) was slowly added to a stirred, cooled (0 °C) solution of 0.80 g (3.6 mmol) of **a** in 18 mL of CH$_2$Cl$_2$. After 1 h, the ice bath was removed and conversion was monitored by ^{31}P{^{1}H} NMR. To the reaction mixture were added 30 mL of CH$_2$Cl$_2$ and 80 mL of degassed, aqueous saturated NaHCO$_3$ solution. The organic layer was separated, and the aqueous layer was extracted with CH$_2$Cl$_2$ (3 × 20 mL). The volume was reduced to 20 mL, and 0.60 g of [Ru(μ-Cl)Cl(η^6-*p*-cymene)]$_2$ (0.99 mmol) was added. After 30 min the conversion was monitored by ^{31}P{^{1}H} NMR and the rest of the [Ru(μ-Cl)Cl(η^6-*p*-cymene)]$_2$ was added (0.275 g, 0.45 mmol). After 30 min 20 mL of water was added. The resulting mixture was extracted with CH$_2$Cl$_2$ (3 × 10 mL) and then evaporated to dryness, affording a crude oil. The pure orange solid (1.46 g, 98%) was obtained after washing repeatedly with acetone and pentane and evaporating to dryness. ^{31}P{^{1}H} NMR (101.2 MHz, C$_6$H$_5$Cl, 298 K; δ (ppm)): 28.1 (s). Typical procedure for the synthesis of complexes **3**: dichloro(κP-η^6-(*R*)-*tert*-butylmethyl(2-phenylethyl)phosphine)ruthenium(II) (**3a**). A 1.49 g portion of **2a** (2.90 mmol) was disolved in chlorobenzene (200 mL). The resulting solution was stirred at 120 °C for 4 h. The product was precipitated by reducing the volume to ca. 100 mL and adding 20 mL of hexane. The precipitate was filtered and washed with pentane. Yield: 0.72 g, 66%. ^{31}P{^{1}H} NMR (101.2 MHz, C$_6$H$_5$Cl, 298 K; δ (ppm)): 61.9 (s). ^{1}H NMR, ^{13}C NMR, IR, and elemental analysis data are given in the Supporting Information.

consists of three sp^3 carbon atoms, is not observed here.[5,15] The benzylic carbon is displaced 0.164 Å from that plane, the phosphorus atom lies at 2.791 Å from the plane, and the chlorine atoms are displaced by 3.201 and 3.176 Å. This shows the distortion that the bidentate ligand generates in the nonregular trigonal geometry of the $RuCl_2P$ fragment.

The molecular structure in the solid state is consistent with the spectroscopic results in solution for **3b**. Thus, the shorter H−H distances between H(1) and H(5) and the hydrogen atoms of the ethylene bridge measured in the solid state are H(7a)−H(5) and H(8b)−H(1) at 2.368 and 2.500 Å, respectively. The combined NOESY and HSQC 2D spectra of **3d** in solution permit the complete assignation of the proton NMR spectrum and confirm that the contacts observed connecting arene and ethylene bridge protons involve the same pairs of hydrogen atoms, H(7a)−H(5) and H(8b)−H(1), which showed shorter H−H distances in the solid state. Therefore, the $[Ru\{\eta^1:\eta^6\text{-}PMe(t\text{-}Bu)(CH_2CH_2(3,5\text{-}Me_2C_6H_3))\}]$ group has a rigid conformation.

The highest ion mass observed in the ESI mass spectra of the ruthenium complexes usually corresponded to the $[M - Cl]^+$ and $[M + CH_3CN - Cl]^+$ fragments when acetonitrile was used as solvent.

To evaluate the discrimination power of the P-stereogenic center in the two remaining coordination positions around the Ru atom, the substitution of one chloro ligand by PPh_3 was studied with **3a**,**b** (eq 3). The stoichiometric reaction is very slow in nonpolar or polar solvents such as CH_2Cl_2 and acetone: 30 h was needed to complete reaction of **3a**,**b** under irradiation with visible light. In the dark the substitution was not observed. Both diastereoisomers were obtained in a constant 3/1 ratio during the reaction. The major diastereoisomer of **4a**,**b** precipitated from the concentrated solution. The NOESY spectra showed contacts between protons of the PPh_3 ligand and *t*-Bu fragment according to an R_PR_{Ru} configuration of the cation complex. In nonpolar solvents such as CH_2Cl_2 and $CHCl_3$ the epimerization of **4a** was not observed after 20 days. However, after 7 days in acetone the amounts of both diastereoisomers of **4b** were similar. The substitution reaction is kinetically controlled, since the more crowded diastereoisomer was obtained in preference.[16] Theoretical calculations are in progress to provide an explanation of the substitution pattern.



(3)

The $^1H-^{19}F$ correlation of a solution of **4a**-R_PR_{Ru} in $CDCl_3$ (HOESY experiment) showed contacts of fluorine with the protons of both the PPh_3 and the *tert*-butyl groups. This is consistent with a position of the PF_6^- anion on the opposite side of the remaining chloro ligand in the ionic pair.

In conclusion, we have obtained a group of P-chiral ligands that allows the synthesis of new tethered phosphinoarene ruthenium complexes. Furthermore, it is possible to introduce elements of planar chirality with complete diastereoselectivity. Work currently in progress is focusing on the preparation of ruthenium complexes containing labile ligands in the coordination sphere and their use as precursors in catalytic processes.

Acknowledgment. This study was supported by the Spanish *Ministerio de Educación y Ciencia* (MEC, project CTQ2007-61058/BQU). R.A. thanks the *DURSI* of the Autonomous Government of Catalonia (*Generalitat de Catalunya*) for the award of a Ph.D. grant.

Supporting Information Available: Text and figures giving experimental information, including details of the syntheses and NMR spectra, and a CIF file giving X-ray structural data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Structure determination of **3b**: molecular weight, 408.29 g/mol; crystal size, 0.2 × 0.1 × 0.1 mm; crystal system, orthorhombic; space group, $P2_12_12_1$; $a = 7.467(3)$ Å, $b = 13.096(4)$ Å, $c = 17.923(4)$ Å, $\alpha = \beta = \gamma = 90.00°$; $V = 1752.7(10)$ Å^3; $Z = 4$; $\rho_{calcd} = 0.946$ g cm^3, $\mu_{lin} = 1.277$ mm^{-1}; $\lambda = 0.710\,73$ Å; $T = 293$ K; 17 326 reflections collected (R(int) = 0.0390); final R indices ($I > 2\sigma(I)$) R1 = 0.0316, wR2 = 0.0864, GOF = 1.178. CCDC 652572 contains the supplementary crystallographic data for this structure. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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