A Chloro-Bridged (Arene)Ru Complex with a Polymerizable Side Chain

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Received September 30, 2002

An $[(arene)RuCl_2]_2$ complex with a methacrylate side chain (**2**) has been prepared in two steps using commercially available starting materials. This complex reacts with PPh_3, pyridine, or toluidine to give the corresponding mononuclear adducts (**3**−**5**). The structure of **4** was determined by single-crystal X-ray diffraction. Complex **2** and the PPh_3 adduct **3** were immobilized by copolymerization with divinylbenzene (DVB) or ethyleneglycol dimethacrylate (EGDMA). The resulting EGDMA copolymer was tested as a catalyst in asymmetric transfer hydrogenations. Using (1*R*,2*R*)-(−)-*N*-*p*-tosyl-1,2-diphenylethylenediamine as the chiral ligand and azeotropic NEt_3/HCO_2H as the reducing agent, aromatic ketones were converted to the corresponding alcohols with selectivities between 87 and 97% ee.

Introduction

Since the first reports on chloro-bridged (arene)Ru^{II} complexes more than 30 years ago,[1] complexes of this kind had a tremendous impact on organometallic synthesis and catalysis. $[(Arene)RuCl_2]_2$ complexes have been employed as catalysts for the conversion of aldoximes to nitriles,[2] for the 1,4-addition of alkynes to conjugated enones,[3] for the hydrolytic oxidation of organosilanes,[4] for hydrosilylations,[5] for arene hydrogenation,[6] for the oxidation of alcohols,[7] and for oxidative Heck reactions.[8] Furthermore, chloro-bridged (arene)-Ru complexes serve as the starting material for the synthesis of many mononuclear catalysts such as [(arene)Ru(L−L′)Cl] (L−L′ = anionic bidentate ligand; transfer hydrogenation,[9] olefin cyclopropanation[10]), $[(arene)Ru(PR_3)Cl_2]$ (ring-opening[11] and ring-closing metathesis,[12] atom transfer radical polymerizations[13]) and $[(arene)Ru(L-L')Cl]^+$ (L−L′ = neutral bidentate ligand; asymmetric Diels−Alder reactions,[14] arene hydrogenation[15]), among others.[16] In view of the potential advantages of heterogeneous as compared to homogeneous catalysts, several groups have investigated methods to immobilize (arene)Ru complexes. In most cases,[17] the attachment to the solid support was achieved by coordination to mono- or bidentate ligands covalently bound to the support (Figure 1, types A and B).[18,19] An attractive alternative is the attachment via the arene π-ligand (Figure 1, types C and D). Here, the same ligands L and L−L′, which have successfully been employed in homogeneous reactions, can be used for the immobilized catalyst. Very recently, complexes of type C have been described for the first time (L = PPh_3 or PCy_3).[20] They were prepared by an arene exchange reaction of $[(C_6H_5CO_2Et)Ru(PR_3)Cl_2]$ with polystyrene and were shown to act as efficient catalysts for ring-closing olefin metathesis reactions. A drawback, however, is that the attachment to the polymer proceeds only under very specific and harsh conditions (120 °C, 24 h).

(1) (a) Winkhaus, G.; Singer, H. *J. Organomet. Chem.* **1967**, *7*, 487−491. (b) Zelonka, R. A.; Baird, M. C. *Can. J. Chem.* **1972**, *50*, 3063−3072. (c) Bennett, M. A.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1974**, 233−241.

(2) Yang, S. H.; Chang, S. *Org. Lett.* **2001**, *3*, 4209−4211.

(3) Chang, S.; Na, Y.; Choi, E.; Kim, S. *Org. Lett.* **2001**, *3*, 2089−2091.

(4) Lee, M.; Ko, S.; Chang, S. *J. Am. Chem. Soc.* **2000**, *122*, 12011−12012.

(5) Na, Y.; Chang, S. *Org. Lett.* **2000**, *2*, 1887−1889.

(6) Fidalgo, E. G.; Plasseraud, L.; Süss-Fink, G. *J. Mol. Catal. A* **1998**, *132*, 5−12.

(7) (a) Lee, M.; Chang, S. *Tetrahedron Lett.* **2000**, *41*, 7507−7510. (b) Karlsson, U.; Wang, G.-Z.; Bäckvall, J.-E. *J. Org. Chem.* **1994**, *59*, 1196−1198.

(8) Farrington, E. J.; Brown, J. M.; Barnard, C. F. J.; Rowsell, E. *Angew. Chem., Int. Ed.* **2002**, *41*, 169−171.

(9) (a) Carmona, D.; Lamata, M. P.; Oro, L. A. *Eur. J. Inorg. Chem.* **2002**, 2239−2251. (b) Noyori, R.; Yamakawa, M.; Hashiguchi, S. *J. Org. Chem.* **2001**, *66*, 2931−2944. (c) Palmer, M. J.; Wills, M. *Tetrahedron: Asymmetry* **1999**, *10*, 2045−2061. (d) Noyori, R.; Hashiguchi, S. *Acc. Chem. Res.* **1997**, *30*, 97−102.

(10) Simal, F.; Demonceau, A.; Noels, A. F. *Tetrahedron Lett.* **1998**, *39*, 3493−3496.

(11) (a) Stumpf, A. W.; Saive, E.; Demonceau, A.; Noels, A. F. *J. Chem. Soc., Chem. Commun.* **1995**, 1127−1128. (b) Hafner, A.; Mühlebach, A.; van der Schaaf, P. A. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2121−2124.

(12) Fürstner, A.; Ackermann, L. *Chem. Commun.* **1999**, 95−96.

(13) (a) Simal, F.; Demonceau, A.; Noels, A. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 538−540. (b) Simal, F.; Sebille, S.; Hallet, L.; Demonceau, A.; Noels, A. F. *Macromol. Symp.* **2000**, *161*, 73−85.

(14) (a) Davies, D. L.; Fawcett, J.; Garratt, S. A.; Russell, D. R. *Organometallics* **2001**, *20*, 3029−3034. (b) Faller, J. W.; Grimmond, B. J. *Organometallics* **2001**, *20*, 2454−2458.

(15) Boxwell, C. J.; Dyson, P. J.; Ellis, D. J.; Welton, T. *J. Am. Chem. Soc.* **2002**, *124*, 9334−9335.

(16) Due to the vast literature on this topic, only selected examples are given.

(17) For a $[(cymene)RuCl_2]_2$ complex on activated carbon see: Choi, E.; Lee, C.; Na, Y.; Chang, S. *Org. Lett.* **2002**, *4*, 2369−2371.

(18) Complexes of type A: (a) Opstal, T.; Melis, K.; Verpoort, F. *Catal. Lett.* **2001**, *74*, 155−159. (b) Leadbeater, N. E.; Scott, K. A.; Scott, L. J. *J. Org. Chem.* **2000**, *65*, 3231−3232. (c) Çetinkaya, B.; Seçkin, T.; Özdemir, I.; Ahci, B. *J. Mater. Chem.* **1998**, *8*, 1835−1838.

(19) Complexes of type B: (a) De Clercq, B.; Lefebvre, F.; Verpoort, F. *New J. Chem.* **2002**, *26*, 1201−1208. (b) Polborn, K.; Severin, K. *Chem. Eur. J.* **2000**, *6*, 4604−4611. (c) Polborn, K.; Severin, K. *Chem. Commun.* **1999**, 2481−2482. (d) Bayston, D. J.; Travers, C. B.; Polywka, M. E. C. *Tetrahedron: Asymmetry* **1998**, *9*, 2015−2018. (e) ter Halle, R.; Schulz, E.; Lemaire, M. *Synlett.* **1997**, 1257−1258. (f) Fan, Q.-H.; Ren, C.-Y.; Yeung, C.-H.; Hu, W.-H.; Chan, A. S. C. *J. Am. Chem. Soc.* **1999**, *121*, 7407−7408.

(20) Akiyama, R.; Kobayashi, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 2602−2604.

10.1021/om020813r CCC: $25.00
Publication on Web 04/01/2003

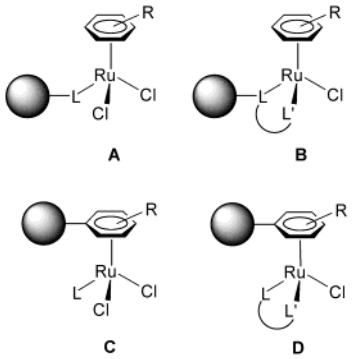
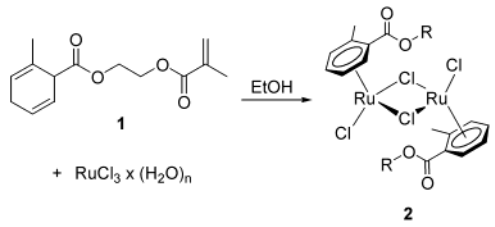


Figure 1. Immobilized (arene)Ru complexes, which are attached to the solid support via mono- or bidentate ligands (A and B) or via the π-ligand (C and D).

Scheme 1. Synthesis of the (Arene)Ru Complex 2 (only one possible diastereoisomer is shown)



To provide a more general access to immobilized catalysts of types C and D, we have investigated whether polymerizable side chains can be attached directly to the arene ring of a chloro-bridged catalyst precursor. The synthesis of a first example of such a complex together with an application in heterogeneous asymmetric catalysis is reported below.

Results and Discussion

The synthesis of the chloro-bridged (arene)Ru complex **2**, having a polymerizable methacrylate side chain attached to the π-ligand, was accomplished in two steps using commercially available starting materials. First, the cyclohexadiene derivative **1** was synthesized by condensation of 2-hydroxyethyl methacrylate with 1,4-dihydro-2-methylbenzoic acid (via the acid chloride). The ester **1** was allowed to react directly with $RuCl_3 \times (H_2O)_n$ without prior purification. The desired chloro-bridged complex **2** crystallizes in 84% yield (Scheme 1).

Since each ruthenium fragment shows planar chirality, the dimeric complex **2** is expected to exist as a mixture of diastereoisomers. The NMR spectra, however, display only one set of signals, presumably due to fast exchange via the kinetically labile chloro bridges. Complex **2** shows the typical reactivity of chloro-bridged complexes: upon reaction with N- or P-donor ligands, the corresponding monomeric adducts **3**−**5** are obtained (Scheme 2).

For complex **4**, the structure in the crystal was determined by X-ray diffraction. A piano stool geometry is observed with bond lengths and angles that are within the expected range (Figure 2). The flexible methacrylate side chain points away from the metal center.

The (arene)Ru complexes described here can easily be incorporated into different polymeric supports. This was demonstrated by copolymerization of **2** or **3** with divinylbenzene (DVB) or with the more polar monomer

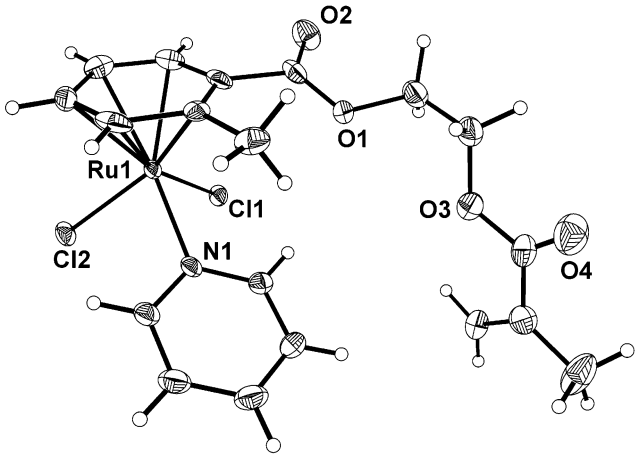


Figure 2. ORTEP[21] representation of the molecular structure of **4** in the crystal. Displacement ellipsoids are drawn at the 40% probability level. Selected bond length (Å) and angles (deg): Ru−N = 2.112(5), Ru−Cl1 = 2.4175-(15), Ru−Cl2 = 2.4063(13); Cl1−Ru−Cl2 = 88.52(5), N−Ru−Cl1 = 86.50(14), N−Ru−Cl2 = 86.35(12).

Scheme 2. Formation of Monomeric Adducts by Reaction with N- or P-Donor Ligands

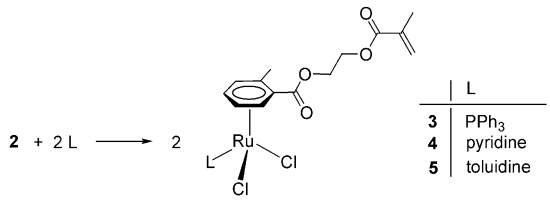


Table 1. Copolymerization of Complexes 2 and 3 with Divinylbenzene or Ethyleneglycol Dimethacrylate

complex	cross-linker	ratio	polymer
2	DVB	1:99	**P1**
2	EGDMA	1:99	**P2**
2	EGDMA	9:91	**P3**
3	DVB	1:99	**P4**
3	EGDMA	1:99	**P5**

ethyleneglycol dimethacrylate (EGDMA) in the presence of $CHCl_3$ using AIBN as the radical initiator (Table 1). We have chosen these comonomers because it was recently shown that the resulting highly cross-linked polymers are well-suited supports for transition metal catalysts.[22] In all cases, the incorporation of the Ru complex was good, as indicated by the nearly colorless washing solution.

To demonstrate that polymers of this kind can be used as heterogeneous catalysts, we have investigated the asymmetric transfer hydrogenation of aromatic ketones. This reaction has received considerable attention in recent years because with (arene)Ru catalysts having

(21) ORTEP 3 for Windows version 1.074. Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.

(22) For some selected examples see: (a) Nestler, O.; Severin, K. *Org. Lett.* **2001**, *3*, 3907−3909. (b) Clapham, B.; Reger, T. S.; Janda, K. D. *Tetrahedron* **2001**, *57*, 4637−4662, and references therein. (c) Taylor, R. A.; Santora, B. P.; Gagné, M. R. *Org. Lett.* **2000**, *2*, 1781−1783. (d) Canali, L.; Cowan, E.; Deleuze, H.; Gibson, C. L.; Sherrington, D. C. *Chem. Commun.* **1998**, 2561−2562. (e) Nozaki, K.; Itoi, Y.; Shibahara, F.; Shirakawa, E.; Ohta, T.; Takaya, H.; Hiyama, T. *J. Am. Chem. Soc.* **1998**, *120*, 4051−4052. (f) Santora, B. P. Larsen, A. O.; Gagné, M. R. *Organometallics* **1998**, *17*, 3138−3140. (g) Salvadori, P.; Pini, D.; Petri, A. *J. Am. Chem. Soc.* **1997**, *119*, 6929−6930.

Scheme 3. Asymmetric Transfer Hydrogenation of Aromatic Ketones Catalyzed by P3/TsDPEN

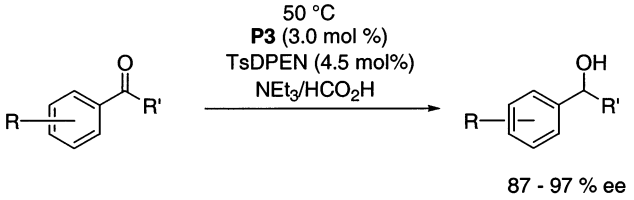


Table 2. Transfer Hydrogenation of Aromatic Ketones Catalyzed by P3/TsDPEN or by 2/TsDPEN

entry	catalyst	substrate	conv (%)[a]	ee (%)[b]
1	**P3**/TsDPEN	acetophenone	82	92
2	**P3**/TsDPEN	*m*-Cl-acetophenone	96	89
3	**P3**/TsDPEN	*m*-F-acetophenone	95	87
4	**P3**/TsDPEN	tetralone	84	97
5	**P3**/TsDPEN	indanone	81	97
6	**2**/TsDPEN	acetophenone	77	94
7	**2**/TsDPEN	*m*-Cl-acetophenone	98	92

[a] The conversion was determined by capillary GC equipped with a CP-cyclodextrin-B-2,3,6-M-19 column. [b] In all cases the main isomer has the configuration *R*.

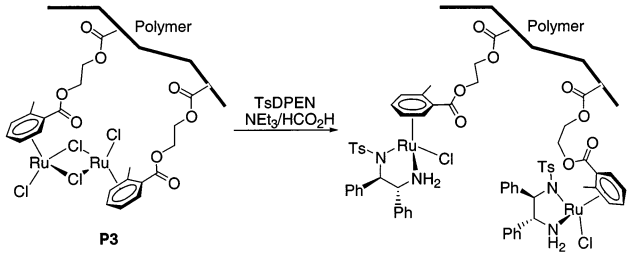
chiral amine-based ligands an excellent enantiomeric excess can be obtained.[9] The combination of (arene)Ru complexes with the ligand *N*-*p*-tosyl-1,2-diphenylethylenediamine (TsDPEN) and azeotropic NEt_3/HCO_2H as the reducing agent, first described by Noyori in 1996,[23] was shown to be especially successful.[24] Immobilized versions of this catalyst have already been described,[19d,e] but here the attachment to the polymer backbone was achieved by employing a functionalized TsDPEN ligand.

Using the polymer **P3** in combination with (1*R*,2*R*)-TsDPEN, we have reduced acetophenone and structurally related ketones (Scheme 3). The reaction was carried out using a catalyst concentration of 3 mol % with respect to the substrate and a slight excess of the chiral ligand (4.5 mol %). The exact ruthenium content of **P3** was determined by ICP analysis.

The results of these reactions are summarized in Table 2 (entries 1−5). For all substrates, the conversion was above 81% and selectivities between 87 and 97% ee were determined. Although these selectivities are good compared to what is found for many other heterogeneous catalysts for the hydrogenation of ketones,[25] they are slightly lower than what is found for reactions catalyzed by the homogeneous catalyst [(*p*-cymene)Ru(TsDPEN−H^+)Cl].[24] Control experiments with the homogeneous catalyst **2** indicate that this is most likely an effect of the different arene π-ligand and not of the immobilization method since values comparable to that of **P3** were obtained (entries 6 and 7).

It should be pointed out that in reactions catalyzed by **P3**, the chiral ruthenium complex is generated in situ on the polymeric support by reaction with the TsDPEN ligand (Scheme 4). The fact that the activities and selectivities obtained for the heterogeneous catalyst **P3** are comparable to those found for the homogeneous catalyst **2** indicates that this functionalization proceeds very efficiently and that the accessibility of the Ru centers in the polymer is very good. It is thus possible to perform bridge-splitting reactions after immobilization of complex **2**, a characteristic that is of importance if other applications are envisioned.

Scheme 4. In Situ Generation of the Active Catalyst by a Bridge-Splitting Reaction between the Immobilized Complex 2 and the Chiral Ligand TsDPEN



The results described above demonstrate that immobilized (arene)Ru complexes can be prepared using **2** as the key starting material. In terms of potential applications in heterogeneous catalysis, this approach shows a number of advantages: (a) Complex **2** is easily accessible using commercially available reagents. (b) The polymeric support can be modified according to specific needs simply by changing the comonomer(s). (c) The desired catalysts can be prepared before or after the immobilization step using the same ligands as in homogeneous reactions. Given these characteristics, it is conceivable that complex **2** will be of interest for many groups working in this field.

Experimental Section

General Procedures. All complexes were synthesized under an inert atmosphere of dinitrogen using standard Schlenk tube techniques. The solvents (analytical grade purity) were degassed and stored under a dinitrogen atmosphere. Divinylbenzene (DVB) (55%, mixture of isomers), ethyleneglycol dimethacrylate (EGDMA), dihydromethylbenzoic acid, (1*R*,2*R*)-(−)-*N*-*p*-tosyl-1,2-diphenylethylenediamine and 2-hydroxyethyl methacrylate were purchased from Aldrich. AIBN was purchased from Fluka and used without further purification. EGDMA was washed with NaOH (1 M) and saturated NaCl solution and dried with Na_2SO_4. After filtration, the monomer was distilled under reduced pressure. Polymerizations were performed in a glovebox containing less than 1 ppm of oxygen and water. The azeotrope of formic acid and triethylamine was obtained by distillation of a 5:2 mixture at 198 °C under atmospheric pressure. The ^1H and ^{13}C spectra were recorded on a Bruker Advance 200 or a Bruker Advance DPX 400 spectrometer using the residual protonated solvents as internal standards. The spectra were recorded at room temperature. The GC analysis was performed with a Varian 3800 spectrometer using a CP-Cyclodextrin-B-2,3,6-M-19 column (50 m). The ICP measurements (inductively coupled plasma) were performed on a Perkin-Elmer ICP-OES 2000 DV instrument.

Ester 1. Oxalyl chloride (1.14 mL, 10.86 mmol) was slowly added to a solution of dihydromethylbenzoic acid (1.00 g, 7.24 mmol) in degassed dichloromethane (30 mL) containing catalytic amounts of DMAP. After heating under reflux for 1 h, the solvent and the excess oxalyl chloride were removed under

(23) Fujii, A.; Hashiguchi, S.; Uematsu, N.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1996**, *118*, 2521−2522.

(24) (a) Alcock, N. J.; Mann, I.; Peach, P.; Wills, M. *Tetrahedron: Asymm.* **2002**, *13*, 2485−2490. (b) Watanabe, M.; Murata, K.; Ikariya, T. *J. Org. Chem.* **2002**, *67*, 1712−1715. (c) Koike, T.; Murata, K.; Ikariya, T. *Org. Lett.* **2000**, *2*, 3833−3836. (d) Mohar, B.; Valleix, A.; Desmurs, J.-R.; Felemez, M.; Wagner, A.; Mioskowski, C. *Chem. Commun.* **2001**, 2572−2573. (e) Okano, K.; Murata, K.; Ikariya, T. *Tetrahedron Lett.* **2000** *41*, 9277−9280. (f) Yamada, I.; Noyori, R. *Org. Lett.* **2000**, *2*, 3425−3427. (g) Murata, K.; Okano, K.; Miyagi, M.; Iwane, H.; Noyori, R.; Ikariya, T. *Org. Lett.* **1999**, *1*, 1119−1121. (h) Vedejs, E.; Trapencieris, P.; Suna, E. *J. Org. Chem.* **1999**, *64*, 6724−6729.

(25) Saluzzo, C.; Lemaire, C. *Adv. Synth. Catal.* **2002**, *344*, 915−928.

reduced pressure. The resulting dihydromethylbenzoic chloride was dissolved in degassed CH_2Cl_2 (20 mL). After addition of NEt_3 (0.10 mL, 0.72 mmol), 2-hydroxyethyl methacrylate (1.06 mL, 8.70 mmol) was added slowly over a period of 15 min. The reaction mixture was subsequently heated under reflux for 6 h. The slightly yellow solution was washed with water and dried over $MgSO_4$. After evaporation of the solvent the product, which contains small amounts of 2-hydroxyethyl methacrylate, was obtained as a slightly yellow oil (yield: 1.63 g, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.71 (s, 3 H, CH_3), 1.93 (s, 3 H, CH_3), 2.72 (m, 2 H, CH_2), 3.63 (m, 1 H, CH), 4.36 (m, 4 H, OCH_2), 5.58 (s, 1 H, C=CH), 5.70 (m, 2 H, CH), 5.88 (m, 1 H, CH), 6.11 (s, 1 H, C=CH). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 18.20 (CH_3), 22.02 (CH_3), 26.75 (CH_2), 47.08 (C_q), 62.31 (CH_2), 62.41 (CH_2), 122.01 (CH), 122.24 (CH), 126.06 (CH), 129.97 (CH), 132.16 (CH), 135.88 (CH), 167.07 (CO), 172.31 (CO).

Complex 2. A solution of $RuCl_3 \times 3H_2O$ (523 mg, 2.00 mmol) and ester **1** (1.50 g, ~6.00 mmol) in degassed ethanol (40 mL) was heated under reflux for 6 h. After evaporation of the solvent under reduced pressure, the residue was extracted with chloroform (30 mL). After evaporation of the solvent, the product was dissolved in a minimum amount of hot ethanol. Cooling to −4 °C gave orange crystals, which were collected and dried (yield: 710 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.97 (s, 6 H, CH_3), 2.48 (s, 6 H, CH_3), 4.51 (m, 4 H, OCH_2), 4.63 (m, 4 H, OCH_2), 5.36 (d, ^3J = 6 Hz, 2 H, CH), 5.60 (s, 2 H, C=CH), 5.73 (t, ^3J = 5 Hz, 2 H, CH), 5.94 (t, ^3J = 5 Hz, 2 H, CH), 6.17 (s, 2 H, C=CH), 6.42 (d, ^3J = 6 Hz, 2 H, CH). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 18.33 (CH_3), 19.75 (CH_3), 62.24 (OCH_2), 64.22 (OCH_2), 65.81, 78.81, 80.54, 88.00, 89.57, 102.93 (CH and C), 126.27 (C=*C*H_2), 135.85 (*C*=CH_2), 165.00 (CO), 167.05 (CO). Anal. Calcd for $C_{28}H_{32}Cl_4O_8Ru_2$: C 40.01, H 3.84. Found: C 39.85, H 3.66.

Complex 3. A solution of the dinuclear complex **2** (50 mg, 60 μmol) and PPh_3 (31 mg, 120 μmol) in degassed dichloromethane (20 mL) was stirred at room temperature for 30 min. After evaporation of the solvent, the product was washed with ether (10 mL). Red-orange needles were obtained by crystallization from ethanol (yield: 56 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.95 (s, 3 H, CH_3), 2.53 (s, 3 H, CH_3), 4.47−4.64 (m, 4 H, OCH_2 and CH), 5.23 (t, ^3J = 5 Hz, 1 H, CH), 5.59 (s, 1 H, C=CH), 6.18 (s, 1 H, C=CH), 6.37 (d, ^3J = 6 Hz, 1 H, CH), 7.37 (m, 9 H, PPh_3), 7.75 (m, 6 H, PPh_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 18.35 (CH_3), 19.56 (CH_3), 62.30 (OCH_2), 63.80 (OCH_2), 80.18, 80.39, 85.45, 88.78, 97.11 (CH and C), 126.37, 128.07, 130.57, 134.11 (PPh_3 and C=CH_2), 164.24 (CO), 167.14 (CO). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 29.26 (s). Anal. Calcd for $C_{32}H_{31}Cl_2O_4PRu$: C 56.31, H 4.58. Found: C 55.99, H 4.78.

Complex 4. The synthesis was performed analogously to that of complex **3** using pyridine (9.7 μL, 120 μmol) instead of PPh_3 (yield: 42 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.95 (s, 3 H, CH_3), 2.31 (s, 3 H, CH_3), 4.47 (m, 2 H, OCH_2), 4.57 (m, 2 H, OCH_2), 5.40 (d, ^3J = 5 Hz, 1 H, CH), 5.61 (s, 1 H, C=CH), 5.63 (t, ^3J = 6 Hz, 1 H, CH), 6.12 (t, ^3J = 6 Hz, 1 H, CH), 6.19 (s, 1 H, C=CH), 6.28 (d, ^3J = 5 Hz, 1 H, CH), 7.32)t, ^3J = 6 Hz, 2 H, CH, pyridine), 7.76 (t, ^3J = 6 Hz, 1 H, CH, pyridine), 8.95 (d, ^3J = 6 Hz, 2 H, pyridine). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 18.29 (CH_3), 19.07 (CH_3), 61.99 (OCH_2), 64.10 (OCH_2), 78.14, 78.43, 81.46, 90.78), 93.56, 104.71 (CH and C), 124.66 (CH, pyridine), 126.67 (C=*C*H_2), 137.91 (*C*=CH_2), 154.89 (CH, pyridine), 165.74 (CO), 167.04 (CO). Anal. Calcd for $C_{19}H_{21}Cl_2NO_4Ru$: C 45.70, H 4.24, N 2.80. Found: C 45.78, H 4.19, N 2.60.

Complex 5. The synthesis was performed analogously to that of complex **3** using toluidine (13 mg, 120 μmol) instead of PPh_3 (yield: 45 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.93 (s, 3 H, CH_3), 2.35 (s, 3 H, CH_3), 2.48 (s, 3 H, CH_3), 4.47−4.56 (m, 4 H, OCH_2), 4.90 (m, 2 H, NH_2), 5.06 (t, ^3J = 5 Hz, 1 H, CH), 5.20 (d, ^3J = 5 Hz, 1 H, CH), 5.59 (s, 1 H, C=CH), 5.72 (t, ^3J = 5 Hz, 1 H, CH), 5.85 (d, ^3J = 5 Hz, 1 H, CH), 6.16 (s, 1 H, C=CH), 7.16 (d, ^3J = 7 Hz, 2 H, CH, toluidine), 7.35 (d, ^3J = 7 Hz, 2 H, CH, toluidine). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 18.32 (CH_3), 19.86 (CH_3), 20.90 (CH_3) 62.09 (OCH_2), 64.27 (OCH_2), 78.58, 78.65, 89.60, 91.47, 103.60 (CH and C), 120.33, 126.51, 129.98, 135.60, 142.40 (toluidine and C=C), 165.93 (CO), 167.17 (CO). Anal. Calcd for $C_{21}H_{25}Cl_2NO_4Ru$: C 47.82, H 4.74, N 2.66. Found: C 47.69, H 4.84, N 2.54.

Polymer P1 and P4. A screw cap vial containing a solution of the (arene)Ru complex **2** or **3** (47.6 μmol), DVB (673 μL, 4.71 mmol), and AIBN (2 wt % relative to monomers) in chloroform (670 μL) was placed in an oil bath (65 °C) for 24 h. The resulting polymer was crushed in a mortar, washed with $CHCl_3$, and dried under vacuum to give an orange powder.

Polymer P2 and P5. A screw cap vial containing a solution of the (arene)Ru complex **2** or **3** (29.3 μmol), EGDMA (549 μL, 2.90 mmol), and AIBN (2 wt % relative to monomers) in chloroform (550 μL) was placed in an oil bath (65 °C) for 24 h. The resulting polymer was crushed in a mortar, washed with $CHCl_3$, and dried under vacuum to give an orange powder.

Polymer P3. A screw cap vial containing a solution of the (arene)Ru complex **2** (146 mg, 174 μmol), EGDMA (337 μL, 1.79 mmol), and AIBN (2 wt % relative to monomers) in chloroform (1.0 mL) was placed in an oil bath (65 °C) for 24 h. The resulting polymer was crushed in a mortar, washed with acetone, and dried under vacuum to give an orange powder. To determine the Ru content, a suspension of the polymer (10 mg) was heated in concentrated sulfuric acid (2 mL) at 150 °C for 2 h. Hydrogen peroxide (30%, 2 mL) was subsequently added, and the mixture was stirred for 48 h at 150 °C. The resulting clear solution was diluted to 10 mL with nitric acid (2%, aqueous) and analyzed by ICP. Result: 4.1 ± 0.5 wt % Ru/polymer.

Asymmetric Transfer Hydrogenation. A suspension/solution of polymer **P3**/complex **2** (12.3 mg/ 2.1 mg, 5 μmol Ru) and TsDPEN ligand (2.8 mg, 7.6 μmol) in formic acid/triethylamine azeotrope (5:2, 0.25 mL) was stirred at 50 °C for 15 min. The reaction was started by addition of the substrate (165 μmol). After 15 h, a sample was removed (10 μL), quenched with acetic acid/acetonitrile (3:1, 800 μL), and analyzed by GC.

Crystallographic Analysis of 4. Crystal data: $C_{19}H_{21}Cl_2NO_4Ru$, M = 499.34, triclinic, space group $P\bar{1}$ (No. 2), a = 7.6540(7) Å, b = 8.3714(8) Å, c = 16.6028(16) Å, α = 79.033(8)°, β = 85.448(8)°, γ = 70.359(9)°, V = 983.49(16) Å^3, Z = 2, D_{calc} = 1.686 g/cm^3, μ = 1.093 mm^{-1}, $F(000)$ = 504, crystal size 0.15 × 0.17 × 0.25 mm^3. Data collection: Oxford Diffraction KM4/Sapphire CCD, T = 140(2) K, Mo Kα radiation, λ = 0.71073 Å, θ 3.58−25.02°, $-7 \le h \le 8$, $-9 \le k \le 9$, $-19 \le l \le 19$, 5948 reflections collected, 3040 independent reflections, R_{int} = 0.0328, 2658 observed reflections [$I > 2\sigma(I)$], semiempirical absorption correction, max./min. transmission 0.8904/0.7718. Refinement: N_{ref} = 3040, N_{par} = 245, R_1 [$I > 2\sigma(I)$] = 0.0419, wR_2 (all data) = 0.1103, S = 1.108, the weighting scheme is $w^{-1} = [\sigma^2(F_o^2) + (0.0447P)^2 + 4.1100P]$ with $P = (F_o^2 + 2F_c^2)/3$, max. and av shift/error = 0.000, 0.000, largest difference peak 1.138 e Å^{-3}, largest difference hole −0.986 e Å^{-3}. Structure solution and refinement by SHELX97 (*Programs for Crystal Structure Analysis*, Sheldrick, G. M., University of Göttingen, Germany, 1998). H atoms were placed in calculated positions using the riding model.

Acknowledgment. The work was supported by the Swiss National Science Foundation and by OMG.

Supporting Information Available: Crystallographic data in CIF format of complex **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020813R