Notes

A Convenient One-Pot Synthesis of a Functionalized-Arene Ruthenium Half-Sandwich Compound $[RuCl_2(\eta^6\text{-}C_6H_5OCH_2CH_2OH)]_2$

Janet Soleimannejad

Department of Chemistry, University of Ilam, Ilam, Iran

Colin White*

Department of Chemistry, The University, Western Bank, Sheffield, U.K., S3 7HF

Received December 4, 2004

Summary: Reaction of $RuCl_3 \cdot xH_2O$ with 1-methoxy-1,4-cyclohexadiene in an alcohol solvent, ROH, gives $[RuCl_2(\eta^6\text{-}C_6H_5OR)]_2$ (R = Me, Et, or $HOCH_2CH_2$) in up to 79% yield. The crystal structures of $[Ru_2(\mu\text{-}Cl_3)(\eta^6\text{-}C_6H_5OEt)_2]^+[BPh_4]^-$ and $[RuCl_2(\eta^6\text{-}C_6H_5OCH_2CH_2OH)]_2$ are also reported.

Introduction

Arene ruthenium half-sandwich compounds have proved to be versatile homogeneous catalysts for a wide range of reactions including alkene[1] and aromatic hydrogenation,[2] asymmetric hydrogen-transfer reduction of ketones[3] and imines,[4] Diels−Alder reactions,[5] and alkene metathesis.[6] They have also been utilized as reagents in organic synthesis.[7] This has stimulated efforts to prepare supported-arene ruthenium complexes in order to have easily recyclable catalysts and reagents.[8] Synthesis of supported complexes would be facilitated if functionalized-arene ruthenium complexes were easily accessible. Further, functionalized-arene ruthenium complexes are also of interest in their own right,[9] in part because they have been shown to be superior catalysts to nonfunctionalized-arene catalysts.[10] However, access to functionalized-arene ruthenium half-sandwich compounds is not trivial. The usual method of synthesising this class of compounds is by dehydrogenation of 1,3- or 1,4-cyclohexadienes using ethanolic $RuCl_3$.[11] This method works well, but for functionalized-arene complexes this route is rarely an option because the required dihydroarene derivatives are usually not available by Birch reduction. An alternative route involves displacement of the cyclooctatriene ligand in Ru(cod)(cot) by an arene under hydrogen,[12] but the limitation of this method is that the cyclooctatriene precursor can be prepared efficiently only on a small scale.[13] More recently, displacement of the labile naphthalene ligand in naphthalene(cyclooctadiene)ruthenium(0) by a functionalized-arene has been the method of choice.[1b,9a] Unfortunately, access to this naphthalene complex requires a three-stage synthesis from $RuCl_3$, and the complex itself is both air-sensitive and thermally unstable. In contrast, the method reported here, a variation of the original synthetic route, provides

* To whom correspondence should be addressed. Tel: 0114 222 9310. Fax: 0114 2229346. E-mail: Colin.white@sheffield.ac.uk.

(1) (a) Moldes, I.; de la Encarnacion, E.; Ros, J.; Alvarez-Larena, A.; Piniella, J. F. *J. Organomet. Chem.* **1998**, *566*, 165. (b) Bennett, M. A. *Coord. Chem. Rev.* **1997**, *166*, 225. (c) Heinemann, F.; Klodwig, J.; Knoch, F.; Wuendisch, M.; Zenneck, U. *Chem. Ber.* **1997**, *130*, 123. (d) Pertici, P.; Vitulli, G.; Bigelli, C.; Lazzaroni, R. *J. Organomet. Chem.* **1984**, *275*, 113.

(2) Wong, T. Y. H.; Pratt, R.; Leong, C. G.; James, B. R.; Hu, T. Q. *Chem. Ind. (Dekker)* **2001**, *82*, 255.

(3) (a) Noyori R.; Yamakawa, M.; Hashiguchi, S. *J. Org. Chem.* **2001**, *66*, 7931. (b) Noyori, R.; Ohkuma, T. *Pure Appl. Chem.* **1999**, *71*, 1493.

(4) (a) Noyori, R.; Hashiguchi, S. *Acc. Chem. Res.* **1997**, *30*, 97. (b) Hashiguchi, S.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1996**, *118*, 4916.

(5) (a) Davenport, A. J.; Davies, D. L.; Fawcett, J.; Russell, D. R. *J. Chem. Soc., Perkin Trans. 1* **2001**, 1500. (b) Davies, D. L.; Fawcett, J.; Garratt, S. A.; Russell, D. R. *Organometallics* **2001**, *20*, 3029. (c) Davenport, A. J.; Davies, D. L.; Fawcett, J.; Garratt, S. A.; Russell, D. R. *J. Chem. Soc., Dalton Trans.* **2000**, 4432.

(6) Jafarpour, L.; Huang, J.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1999**, *18*, 3760.

(7) (a) Pigge, F. C.; Coniglio, J. J. *Curr. Org. Chem.* **2001**, *5*, 757. (b) Pearson, A. J.; Lee, K. *J. Org. Chem.* **1994**, *59*, 2304.

(8) (a) Sandee, A. J.; Petra, D. G.; Reek, J. N.; Kamer, P. C.; van Leeuwen, P. W. *Chemistry* **2001**, *7*, 1202. (b) Leadbeater, N. E.; Scott, K. A.; Scott, L. J. *J. Org. Chem.* **2000**, *65*, 3231. (c) Bayston, D. J.; Travers, C. B.; Polywka, M. E. C. *Tetrahedron Asym.* **1998**, *9*, 2015. (d) Ciardelli, F.; Pertici, P. *Z. Naturforsch. B Anorg. Chem., Org. Chem.* **1985**, *40B*, 133.

(9) (a) Bodes, G.; Heinemann, F. W.; Marconi, G.; Neumann, S.; Zenneck, U. *J. Organomet. Chem.* **2002**, *641*, 90. (b) Nelson, J. H.; Ghebreyessus, K. Y.; Cook, V. C.; Edwards, A. J.; Wielandt, W.; Wild, S. B.; Willis, A. C. *Organometallics* **2002**, *21*, 1727. (c) Bennett, M. A.; Edwards, A. J.; Harper, J. R. Khimyak, T.; Willis, A. C. *J. Organomet. Chem.* **2001**, *629*, 7. (d) Miyaki, Y.; Onishi, T.; Kurosawa, H. *Inorg. Chim. Acta* **2000**, *300−302,* 369. (e) Brunner, H.; Valerio, C.; Zabel, M. *New J. Chem.* **2000**, *24*, 275. (f) Therrien, B.; Koenig, A.; Ward, T. R. *Organometallics* **1999**, *18*, 1565.

(10) (a) Cetinkaya, B.; Demir, S.; Ozdemir, I.; Toupet, L.; Semeril. D.; Bruneau, C.; Dixneuf, P. H. *New J. Chem.* **2001**, *25*, 519. (b) Miyaki, Y.; Onishi, T.; Ogoshi, S.; Kurosawa, H. *J. Organomet. Chem.* **2000**, *616*, 135. (c) Simal, F.; Jan, D.; Demonceau, A.; Noels, A. F. *Tetrahedron Lett.* **1999**, *40*, 1653.

(11) (a) Pertici, P.; Salvadori, P.; Biasci, A.; Vitulli, G.; Bennett, M. A.; Kane-Maguire, L. A. P. *J. Chem. Soc., Dalton Trans.* **1988**, 315. (b) Bennett, M. A.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1974**, 233. (c) Zelonka, R. A.; Baird, M. C. *Can. J. Chem.* **1972**, *50*, 3063. (d) Winkhaus, G.; Singer, H. *J. Organomet. Chem.* **1967**, *7*, 487.

(12) Pertici, P.; Vitulli, G.; Lazzaroni, R.; Salvadori, P.; Barili, P. L. *J. Chem. Soc., Dalton Trans.* **1982**, 1019.

(13) Bennett, M. A.; Neumann, H.; Thomas, M.; Wang, X. Q.; Pertici, P.; Salvadori, P.; Vitulli, G. *Organometallics* **1991**, *10*, 3238.

10.1021/om049044x CCC: $30.25
Publication on Web 04/07/2005

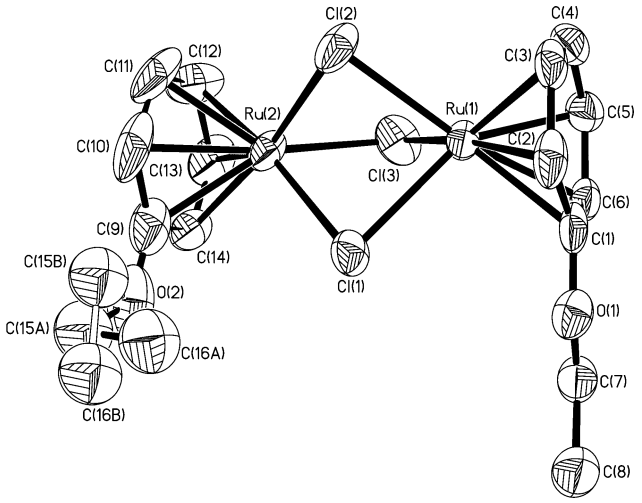

Figure 1. Molecular structure of $[Ru_2(\eta^6\text{-}C_6H_5OCH_2CH_3)_2(\mu\text{-}Cl)_3]^+$ cation, **3** (thermal ellipsoids at 50% probability). Solvate acetone and hydrogen atoms have been omitted for clarity.

access to a functionalized-arene ruthenium complex in one step using hydrated $RuCl_3$.

Results and Discussion

1-Methoxy-1,4-cyclohexadiene is commercially available and, as reported previously,[11b] refluxing this with hydrated ruthenium trichloride in methanol affords $[RuCl_2(\eta^6\text{-}C_6H_5OCH_3)]_2$ (**1**) in 44% yield. If, however, the reaction is carried out in ethanol, then $[RuCl_2(\eta^6\text{-}C_6H_5OEt)]_2$ (**2**) is obtained as an orange-brown solid in 61% yield (Scheme). This compound was fully characterized by elemental analysis and spectroscopic methods; in particular, the presence of the ethoxy group was evident in the ^{1}H NMR spectrum from the characteristic quartet at δ 4.23 and a triplet at δ 1.45 ppm. However, given the unusual synthetic route, we wished to confirm the product identity unambiguously by X-ray crystallography. Unfortunately, the product was not very soluble and attempts to grow suitable crystals were unsuccessful, but addition of $NaBPh_4$ to a dilute ethanolic solution of the product gave a yellow precipitate that readily crystallized from acetone. Spectroscopic and X-ray[14] analyses of these crystals revealed that they were tri-μ-chlorobis(η^6-ethoxybenzene)diruthenium(1+) tetraphenylborate (**3**) (Figure 1), confirming that alkoxide exchange had taken place; clearly the ethoxide had originated from the reaction solvent, ethanol. This immediately suggested a route to functionalized-arene complexes, and we were delighted to find that repeating the reaction in 1,2-ethanediol at 80 °C gave the corresponding $[RuCl_2(\eta^6\text{-}C_6H_5OCH_2CH_2OH)]_2$ complex **4** in 79% yield (Scheme 1). Elemental analysis and spectroscopy supported this formulation, which was confirmed by X-ray crystallography. The crystallographic details and selected bond distances and angles for both structures are given in Tables 1 and 2, respectively. An interesting feature of the structure of **4** is that the 2-hydroxyethoxy substituents lie on opposite sides of the molecule as far apart as possible (Figure 2); the same is not true for the ethoxy substituents in **3**.

(14) Sheldrick, G. M. *SHELXL-97*, Program for crystal structure refinement; University of Göttingen: Göttingen, Germany, 1997.

Scheme 1

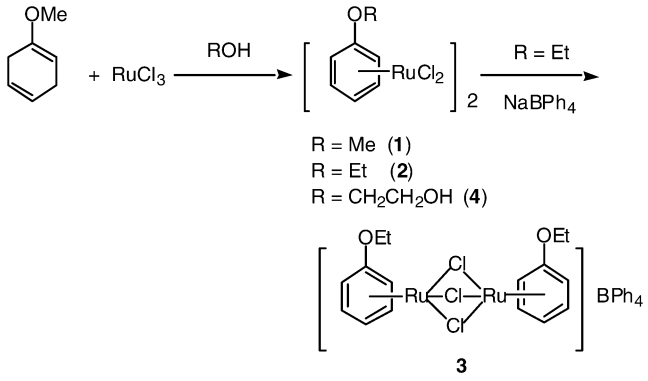

Table 1. Crystal Data and Structure Refinement Details

	3	**4**
formula	$C_{40}H_{40}BCl_3O_2Ru_2 \cdot C_3H_6O$	$C_{16}H_{20}Cl_4O_4Ru_2$
formula wt	930.10	620.26
cryst dimens/mm	0.43 × 0.22 × 0.13	0.14 × 0.12 × 0.08
wavelength, Å	0.71073	0.71073
cryst syst	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$
a, Å	10.0185(12)	6.149(3)
b, Å	17.180(2)	9.548(4)
c, Å,	23.544(3)	9.604(5)
α, deg	90	116.519(11)
β, deg	98.977(3)	108.648(9)
γ, deg	90	91.492(8)
V, Å^3	4002.7(8)	468.4(4)
Z	4	1
D_c, Mg/m^3	1.543	2.199
abs coeff, mm^{-1}	0.993	2.203
F(000)	1888	304
θ range, deg	1.47−28.38	2.43−28.37
index ranges	$-11 \le h \le 11$, $-19 \le k \le 20$, $-26 \le l \le 27$	$-4 \le h \le 7$, $-11 \le k \le 10$ $-11 \le l \le 11$
no of rflns	21 238	2335
no of indep rflns	7008 ($R_{(int)} = 0.0457$)	1622 ($R_{(int)} = 0.0619$)
no of data/restraints/params	7008/47/503	1622/55/118
goodness of fit on F^2	0.976	0.950
final R indices ($I > 2\sigma(I)$)	R1 = 0.0443, wR2 = 0.1208	R1 = 0.0727, wR2 = 0.1857
largest diff peak and hole, e Å^{-3}	1.072 and −0.552	1.358 and −2.053

Table 2. Selected Bond Distances (Å) and Angles (deg) for 3 and 4

3		**4**	
Ru(1)−C(1)	2.254(5)	Ru(1)−C(1)	2.171(13)
Ru(1)−C(2)	2.172(5)	Ru(1)−C(2)	2.136(12);
Ru(1)−C(3)	2.162(4)	Ru(1)−C(3)	2.155 (12)
Ru(1)−C(4)	2.167(5)	Ru(1)−C(4)	2.144(14)
Ru(1)−C(5)	2.152(5)	Ru(1)−C(5)	2.159(14)
Ru(1)−C(6)	2.180(4)	Ru(1)−C(6)	2.199(12)
Ru(1)−Cl(1)	2.4512 (13)	Ru(1)−Cl(1)	2.390(4)
Ru(1)−Cl(2)	2.4095(13)	Ru(1)−Cl(2)	2.418(3)
Ru(1)−Cl(3)	2.4328(14)	Ru(1)−Cl(2A)	2.423(3)
Cl(2)−Ru(1)−Cl(1)	79.83(5)	Cl(1)−Ru(1)−Cl(2)	86.85(13)
Cl(3)−Ru(1)−Cl(1)	79.38(5)	Cl(1)−Ru(1)−Cl(2A)	87.44(12)
Cl(2)−Ru(1)−Cl(3)	80.66(5)	Cl(2)−Ru(1)−Cl(2A)	81.50(12)
Ru(1)−Cl(1)−Ru(2)	83.55(4)	Ru(1)−Cl(2)−Ru(1A)	98.50(12)
Ru(1)−Cl(2)−Ru(2)	84.78(4)		
Ru(1)−Cl(3)−Ru(2)	84.36(5).		

We were obviously intrigued by the mechanism of these unexpected reactions. It was readily shown that the coordinated arene does not undergo alkoxy ex-

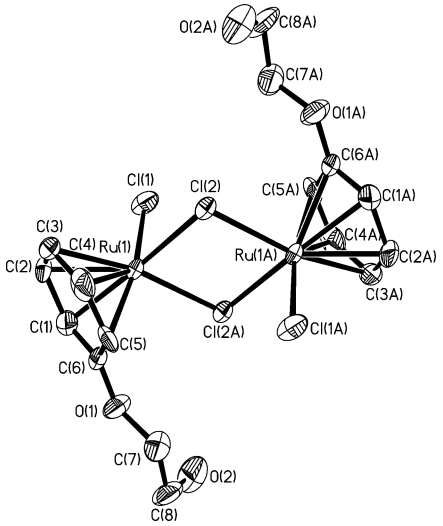

Figure 2. Molecular structure of $[Ru(\eta^6\text{-}C_6H_5OCH_2CH_2OH)Cl_2]_2$, **4** (thermal ellipsoids at 50% probability). Hydrogen atoms have been omitted for clarity.

change. Thus, heating $[RuCl_2((\eta^6\text{-}C_6H_5OCH_3)]_2$ under reflux in ethanol for 9 h did not lead to the formation of $[RuCl_2((\eta^6\text{-}C_6H_5OCH_2CH_3)]_2$; similarly, heating $[RuCl_2((\eta^6\text{-}C_6H_5OCH_2CH_2OH)]_2$ in methanol under reflux for 9 h did not lead to the formation of $[RuCl_2((\eta^6\text{-}C_6H_5OCH_3)]_2$, and conversely heating $[RuCl_2((\eta^6\text{-}C_6H_5OCH_3)]_2$ in 1,2-ethanediol at 80 °C for 9 h did not lead to $[RuCl_2((\eta^6\text{-}C_6H_5OCH_2CH_2OH)]_2$. In all cases the original arene complex was recovered unchanged, as confirmed by ^{1}H NMR spectroscopy. We therefore suspected a ruthenium-catalyzed reaction but found that *ruthenium is not necessary for alkoxy exchange to take place.* This was shown by heating 1-methoxy-1,4-cyclohexadiene in 1,2-ethanediol at 80 °C for 9 h and analyzing the mixture by GC-MS. 2-Hydroxyethoxycyclohexadiene was found to be a major component of the reaction mixture; control experiments showed that this was absent in the original 1-methoxy-1,4-cyclohexadiene. A similar experiment with $RuCl_3$ present resulted in a much more complex mixture. Again 2-hydroxyethoxycyclohexadiene was present, together with disproportionation products, i.e., arenes and cyclohexenes and some oligomers. It is significant that there are many reports in the literature of the synthesis of ruthenium arene complexes from simple dienes that are carried out in alcoholic solvents, and in no case has it been reported that alkoxy-arene complexes are formed. This clearly indicates that the exchange is promoted by the methoxy group in the diene. It is known that enol ethers readily undergo acid-catalyzed alkoxy exchange,[15] and in the syntheses reported here the source of the proton could be hydrated ruthenium trichloride; further, as the experiments carried out in the absence of ruthenium show, the alcohol solvent can also be a proton source.

In the synthesis of **1**, **2**, and **4** a minor byproduct, formed in up to 5% yield, was $[RuCl_2(\eta^6\text{-}C_6H_6)]_2$ (**5**).[11b] Ruthenium hydrides are clearly formed in the process of dehydrogenating the 1-alkoxy-1,4-cyclohexadiene to an arene. Thus, 1,4-cyclohexadiene, the precursor to the benzene ligand in **5**, could be formed by a similar acid-catalyzed mechanism to the alkoxy exchange discussed above, but in this case the attacking nucleophile will be H^- rather than OR^-. This suggests that the reaction could be modified using other nucleophiles to enable other functionalized-arene complexes to be synthesized. Unfortunately, however, this reaction does not seem to be as general as we would have hoped in that we have failed to isolate any products using $HOCH_2CH{=}CH_2$, $HOCH_2CH_2NH_2$, or $HOCH(Me)CO_2Et$ as the alcohol. We presume that in these cases the additional functionality interferes with complexation of the diene to ruthenium. Surprisingly, replacing $HOCH_2CH_2OH$ with $HOCH_2CH_2CH_2OH$ results in a dramatic reduction in the yield of product. The reaction does, however, proceed well with $HOCH_2CH(Et)OH$ to give a mixture of products resulting from reaction predominantly, but not exclusively, at the primary alcohol site. Despite these restrictions, others have shown that the functionality in the side chain of arene-ruthenium complexes can be readily modified.[9a,b,d,16] Thus, the synthesis reported here provides a significant breakthrough for the ready synthesis of functionalized-arene ruthenium half-sandwich compounds.

Experimental Section

All reactions were carried out under nitrogen using Schlenk techniques, but the workup was performed in air. All reagents and solvents were obtained commercially and were degassed but used without further purification. NMR spectra were recorded with a Bruker AM250 spectrometer operating at 250.13 MHz (^{1}H) or at 62.90 MHz (^{13}C) using the ^{2}D-lock signal as an internal reference. Mass spectra were recorded using a Fisons VG Prospec 8 spectrometer. Elemental analyses were performed by the Microanalytical Services of the Chemistry Department, University of Sheffield.

Synthesis of $[Ru(\eta^6\text{-}C_6H_5OCH_2CH_3)Cl_2]_2$, 2 A solution of ruthenium trichloride trihydrate (1.0 g, 3.82 mmol) and 1-methoxy-1,4-cyclohexadiene (2.7 mL, 23 mmol) in ethanol (50 mL) was heated under reflux for 8 h. On standing overnight at room temperature, a dark green precipitate separated out. This was filtered off, and the product was extracted from the residue with chloroform using a Soxhlet extractor. The chloroform was removed in vacuo and the residue washed with diethyl ether (3 × 20 mL) to leave a bright orange solid. Additional product was also obtained by reducing the volume of the original ethanol filtrate to approximately half and refrigerating overnight (total 0.69 g, 61%). Anal. Calcd for $C_{16}H_{20}Cl_4O_2Ru_2$: C, 32.7; H, 3.4; Cl, 24.1. Found: C, 32.1; H, 3.4; Cl, 24.1. ^{1}H NMR (d_6-DMSO): δ 1.45 (t, 6 H, *Me*, J = 6.7 Hz), 4.23 (q, 4 H, q, *CH*$_2$), 5.46 (t, 2 H, *Ph,* J = 5.3 Hz), 5.55 (d, 4 H, *Ph,* J = 6.4 Hz), 6.36 (t, 4 H, *Ph,* J = 5.9 Hz). ^{13}C NMR (d_6-DMSO): δ 14.6 (2 C, *Me*), 65.8 (4 C, *Ph*), 66.4 (2 C, -*OCH*$_2$), 74.7 (2 C, *Ph*), 94.6 (4 C, *Ph*), 140.5 (2 C, O*Ph*). *m/z* (FAB+): 555 ([M$^+$] − Cl, 100%).

Synthesis of $[Ru_2(\eta^6\text{-}C_6H_5OCH_2CH_3)_2(\mu\text{-}Cl)_3][BPh_4]$, 3. $NaBPh_4$ (0.23 g, 0.67 mmol) was added to $[RuCl_2(\eta^6\text{-}C_6H_5OC_2H_5)]_2$ (0.20 g, 0.33 mmol) dissolved in ethanol (25 mL) and the resulting mixture stirred overnight. The solvent was evaporated off, and the residual solid was recrystallized from acetone to afford the title compound as yellow crystals (0.23 g, 80%). Anal. Calcd for $C_{40}H_{40}BCl_3O_2Ru_2\cdot(CH_3)_2CO$: C, 55.5; H, 5.0; Cl, 11.4. Found: C, 55.4; H, 4.9; Cl, 11.6. ^{1}H NMR (d_6-acetone): δ 1.45 (t, 6 H, OCH_2CH_3, J = 7.0 Hz), 4.28 (q, 4 H, OCH_2CH_3), 5.54 (t, 2 H, *Ph*OEt, J = 5.4 Hz), 5.62 (d, 4 H, *Ph*OEt, J = 6.4 Hz), 6.15 (4 H, t, *Ph*OEt, J = 5.9 Hz), 6.75 (m, 4 H, *BPh*$_4$), 6.92 (m, 8 H, *BPh*$_4$), 7.32 (m, 8 H, *BPh*$_4$). ^{13}C NMR (d_6-acetone): δ 14.6 (2 C, *Me*), 61.8 (4 C, *Ph*OEt), 67.7 (2 C,

(15) Effenberger, F. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 295.

(16) Pearson, A. J.; Hwang, J. J. *J. Org. Chem.* **2000**, *65*, 3466.

OCH₂), 71.8 (2 C, *Ph*OEt), 85.2 (4 C, *Ph*OEt), 122.3, 126.1, 137.0 (22 C, O*Ph, BPh₄*), 206.3 (4 C, *BPh₄*). *m/z* (FAB+): 555 ([M⁺] − BPh_4, 100%).

Synthesis of [Ru(η^6-$C_6H_5OCH_2CH_2OH$)Cl_2]$_2$, 4. A mixture of ruthenium trichloride trihydrate (1.0 g, 3.82 mmol) and 1-methoxy-1,4-cyclohexadiene (4.5 mL, 38.4 mmol) in 1,2-ethanediol (15 mL) was heated to 80 °C for 3 h. On standing overnight at room temperature, a red-orange precipitate separated out. This was filtered off, washed with methanol, and dried in vacuo (0.78 g, 66%). Additional product was obtained by evaporating under reduced pressure the original filtrate to approximately a third of the volume (total 0.93 g, 79%). Anal. Calcd for $C_{16}H_{20}Cl_4O_4Ru_2$: C, 31.0; H, 3.2; Cl, 22.9. Found: C, 31.0; H, 3.1; Cl, 22.5. ^{1}H NMR (d_6-DMSO): δ 3.72 (t, 4 H, *CH₂*, J = 5.0 Hz), 4.21 (t, 4 H, *CH₂*), 5.37 (t, 2 H, *Ph*, J = 5.3 Hz), 5.56 (d, 4 H, *Ph,* J = 6.4 Hz), 6.15 (t, 4 H, *Ph,* J = 5.8 Hz). ^{13}C (d_6-DMSO): δ 59.4 (2 C, *CH₂*), 65.9 (4 C, *Ph*), 72.0 (2 C, *CH₂*), 74.8 (2 C, *Ph*), 94.5 (4 C, *Ph*), 163.5 (2 C, *PhO*). *m/z* (ES+): 275 ([M⁺]/2 − Cl, 38%), 239 ([M⁺]/2 − 2Cl, 100%).

Crystallographic Analysis of [Ru_2(η^6-$C_6H_5OCH_2CH_3$)$_2$(μ-Cl)$_3$][BPh_4], 3, and [Ru(η^6-$C_6H_5OCH_2CH_2OH$)Cl_2]$_2$, 4. Crystals of **3** and **4** suitable for X-ray diffraction were grown from acetone. These were mounted on a glass fiber with epoxy resin. Data for both structures were collected at 150(2) K using a Bruker SMART1000 CCD area detector. Empirical absorption corrections were employed. The structures were solved by direct methods (SHELXL-97)[14] and refined using least-squares methods on F^2. A summary of the crystallographic data is given in Table 1. In **3** the atoms of the sidearm, C(15) and C(16), were found to be disordered and refined to an occupancy of 60%−40%. The oxygen atom of the solvent molecule, O(3), also appeared to be disordered and placed to an occupancy of 52%−48%. Additional data on the collection of the data and the refinement of the structures are available in the Supporting Information.

Acknowledgment. We are grateful to Johnson Matthey for the generous loan of ruthenium salts (to C.W.).

Supporting Information Available: Tables containing complete crystal and data collection parameters and positional parameters for **3** and **4**. Crystal data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

OM049044X