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2,5-Dimethyl-3,4-bis[(2*R*,5*R*)-2,5-dimethylphospholano]thiophene: First Member of the Hetero-DuPHOS Family

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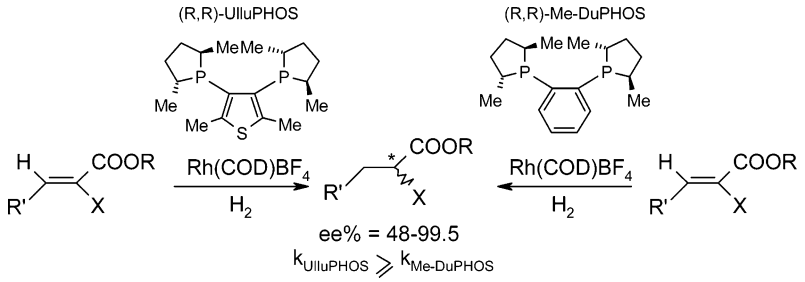

The 2,5-dimethyl-3,4-bis[(2*R*,5*R*)-2,5-dimethylphospholano]thiophene (UlluPHOS), a new thiophene-based analogue of (*R*,*R*)-1,2-bis(phospholano)benzene (Me-DuPHOS), was synthesized, geometrically and electronically characterized, and employed as ligand of Rh and Ru in some standard hydrogenation reactions of prostereogenic functionalized carbon−carbon and carbon−oxygen double bonds. The synthesis of UlluPHOS is much easier than that provided for Me-DuPHOS. UlluPHOS and Me-DuPHOS display very similar geometries, while the electronic availability of the former is higher than that exhibited by the latter. The Rh and Ru complexes of UlluPHOS produced excellent enantiomeric excesses (98.9−99.5%) in the hydrogenation of *N*-acetyl-α-enamino acids and reaction rates higher than those found when employing the analogous complexes of Me-DuPHOS.

Introduction

We previously conceived and demonstrated the utility of five-membered aromatic heterocycles as multifunctional scaffolds for the phosphorus atoms of chiral diphosphine ligands.[1] The use of heterocyclic aromatic systems as a ligand scaffold engenders substantial synthetic advantages over carbocyclic aromatic analogues. In addition, and perhaps more importantly, heteroaromatic scaffolds allow fine modulation of the electronic properties of the chelating functions bound to the heterocyclic ring. Electronic tuning at phosphorus can be performed either by using different aromatic heterocycles or by changing the position of the phosphine group on a given heterocyclic system. This makes it possible to select the ligand having the electronic properties that can better satisfy the requirements imposed by the reaction typology and by the substrate. For example, electron-rich ligands have been observed to elevate both stereoselectivity and rate of hydrogenation reactions involving prostereogenic carbon−oxygen[2] and carbon−carbon functionalized double bonds. Similar results also were reported for Diels−Alder [4 + 2]cycloaddition reactions.[3] By contrast, certain car-

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[||] Diversa Corp.
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[#] Studio di Consulenza Scientifica.

(1) (a) Benincori, T.; Brenna, E.; Sannicolò, F.; Trimarco, L.; Antognazza, P.; Cesarotti, E. *J. Chem. Soc. Chem. Commun.* **1995**, 685−686. (b) Benincori, T.; Brenna, E.; Sannicolò, F.; Trimarco, L.; Antognazza, P.; Cesarotti, E.; Demartin, F.; Pilati, T. *J. Org. Chem.* **1996**, *61*, 6244-. (c) Benincori, T.; Brenna, E.; Sannicolò, F.; Trimarco, L.; Antognazza, P.; Cesarotti, E.; Demartin, F.; Pilati, T.; Zotti, G. *J. Organomet. Chem.* **1997**, *529*, 445−453. (d) Benincori, T.; Cesarotti, E.; Piccolo, O.; Sannicolò, F. *J. Org. Chem.* **2000**, *65*, 2043−2047. (e) Benincori, T.; Rizzo, S.; Sannicolò, F. *J. Heterocycl. Chem.* **2002**, *39*, 471−485.

(2) Benincori, T.; Piccolo, O.; Rizzo, S.; Sannicolò, F. *J. Org. Chem.* **2000**, *65*, 8340−8347.

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bon−carbon bond forming reactions are favored by catalysts resulting from ligands that are relatively electron-deficient.[4]

To quantitatively evaluate the electron-donor ability of ligands, among the many parameters available, we have chosen the electrochemical oxidation peak potential ($E°_p$, volt) determined by voltammetry. In some cases, we have been able to find quantitative relationships between the $E°_p$ values of the free ligands and the catalytic activity exhibited by their metal complexes.[2]

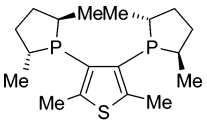
The strategy of using five-membered heteroarenes as scaffolds for different chelating functions (e.g. phosphinooxazoline) has become rather popular in the past few years, and recent literature has been enriched with many chiral ligands bearing electron-donor groups supported by heteroaromatic scaffolds.[5] We considered extending the strategy to the very successful class of DuPHOS ligands, which bear the five-membered phospholane moiety as the stereogenic component.[6] An academic−industrial cooperative effort was initiated in 1999 to test the concept and to design and investigate this new class of modular ligands containing phospholanes attached to heteroaromatic backbones.

Results and Discussion

This paper reports the synthesis, structural characterization, and some preliminary applications of (*R*,*R*)-2,5-dimethyl-[3,4-bis(2′,5′-dimethylphospholanyl)]-thiophene (**1**, UlluPHOS). This diphosphine is the first member of a new family of C_2 symmetric hetero-DuPHOS ligands, characterized by the presence of two homomorphic chiral 2,5-dimethyl-substituted phospholane groups, bound to the homotopic ortho positions of a five-membered aromatic heterocycle.[7]

The basic guidelines for our design are the following: (i) We considered as a crucial point that the ligand would be electron-rich, since, as anticipated, large electronic availability at phosphorus is a prerequisite for fast kinetics in certain hydrogenation processes. Thus, we chose the electron-rich thiophene ring as the scaffold for the phospholane units. We located the phosphacycles in the β-positions, which are endowed with much higher electron density than the α-positions.[8] (ii) We considered that it was a great advantage to maintain the homotopism of the phospholane units, since the metal complexes resulting from asymmetric ligands, displaying phosphine units located in electronically and constitutionally different surroundings, have not proven as effective at inducing high levels of absolute stereocontrol as C_2 symmetric versions.[9] (iii) The two methyl groups in the α- and α′-positions have multiple functions. Since the construction of the phospholane rings involves double lithiation at phosphorus of a 3,4-thienylidenenediphosphine, the methyl groups guard against possible alternative α,α′-ring lithiation. Furthermore, they could increase the electronic availability of the thiophene ring and hence of the phosphorus atoms. Additional, unpredictable effects could also result from steric interactions between the methyl groups and the phospholane units, thus reducing the conformational mobility of the ligand.

SCHEME 1. (*R*,*R*)-2,5-Dimethyl-[3,4-bis(2′,5′-dimethylphosphospholanyl)]thiophene



1
(R,R)-UlluPHOS

The synthesis of **1**, outlined in Scheme 2, follows the sequence employed for preparing the phospholane rings of Me-DuPHOS, starting from an *o*-arylidene diphosphine and the cyclic sulfate of enantiopure 2,5-hexanediol. The preparation of the 2,5-thienylene diphosphine (**2**) takes advantage of the palladium-mediated reaction of easily available 3,4-diiodo-2,5-dimethylthiophene[10] with triethyl phosphite, giving diphosphonate **3** in fairly good yields. This synthesis is easier than that described for *o*-phenylenediphosphine, which involves a sequence of experimentally critical steps: the double metalation of *o*-dichlorobenzene with butyllithium, the quenching of the resulting ortho-dianion with highly reactive and aggressive bis(diethylamino)chlorophosphine, and the reaction of the product with dry hydrogen chloride.[6,11]

To structurally characterize (*R*,*R*)-UlluPHOS (**1**) and evaluate the geometric properties of this new ligand when coordinated to a metal center, we have obtained crystals of the (1,5-cyclooctadiene)−rhodium(I)−tetrafluoborate complex (**4a**) suitable for single-crystal X-ray diffractometric analysis. An ORTEP diagram displaying a projection from above the square plane of the complex is shown in Figure 1a. For comparison, the projection of the analogous [((*S*,*S*)-Me-DuPHOS)Rh(1,5-cyclooctadiene)]-SbF_6 complex, is provided in Figure 1b.[6]

Table 1 summarizes some of the most characteristic structural data of these complexes.

From these data it can be inferred that the geometries of the UlluPHOS and Me-DuPHOS stereogenic core in the solid state are nearly superimposable. Taking the plane of the aromatic rings as a reference plane, an identical out-of-plane distortion of the rhodium and phosphorus atoms is observed in both the complexes.

(3) Celentano, G.; Benincori, T.; Radaelli, S.; Sada, M.; Sannicolò, F. *J. Organomet. Chem.* **2002**, *643*−*644*, 424−430.

(4) (a) Tietze, L. F.; Thede, K. *J. Chem. Soc. Chem. Commun.* **1999**, 1811−1812: (b) Tietze, L. F.; Thede, K.; Sannicolò, F.; Schimpf, R. *J. Chem. Soc. Chem. Commun.* **2000**, 583−584.

(5) Tietze, L. F.; Lohmann, J. K. *Synlett* **2002**, 2083−2085.

(6) Burk, J. M.; Feaster, J. E.; Nugent, W. A.; Harlow, R. L. *J. Am. Chem. Soc.* **1993**, *115*, 10125−10138.

(7) Sannicolò, F.; Piccolo, O.; Benincori, T.; Sada, M.; Verrazzani, A.; Tollis, S.; Ullucci, E.; De Ferra, L.; Rizzo, S. Patent WO03074169; Patent EP1490173.

(8) Some ligands displaying two homomorphic phospholane units bound to the 2,3-positions of electron-poor thianaphthene have been prepared by a past co-worker of one of us and patented by Solvias. These diphosphines are asymmetric, since the two phospholane rings are located on constitutionally heterotopic carbon atoms.

(9) Degussa patented and currently commercializes through Strem Chemicals, Inc. (Bischheim, 67800, France) a couple of C_2 symmetric bis(phospholane) ligands characterized by nonaromatic, very electron poor maleic anhydride and maleinimide as scaffolds for the phospholane rings. Patent WO03084971.

(10) ,5-Dimethyl-3,4-diiodothiophene is the starting material employed to prepare the tetraMe-BITIOP, a chiral biheteroaromatic ligand,[1d] currently produced at a kiloscale level at Chemi S.p.A.

(11) Diphosphinobenzene can be also prepared on a scale through a photochemical reaction between dichlorobenzene and trimethyl phosphite, followed by reduction with LAH/TMSCl (see: Kyba et al. *Organometallics* **1983**, *2*, 1877−1879).

SCHEME 2. Synthetic Schemes for UlluPHOS (1) and Me-DuPHOS

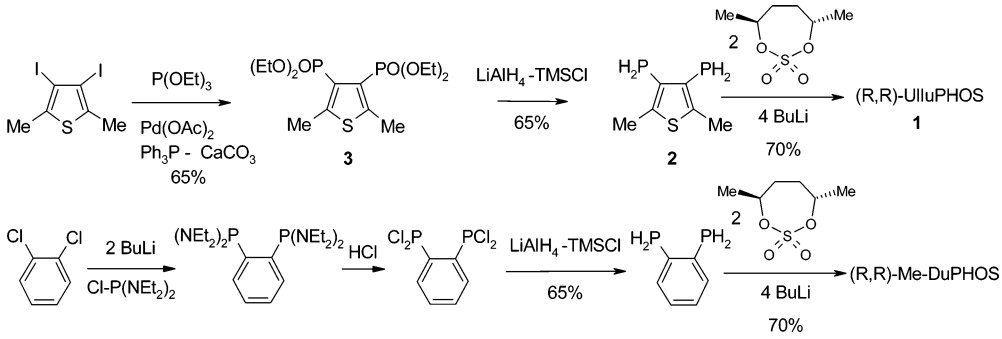


TABLE 1. Comparison of Some Bond Angles (θ_i), Bond Lengths (l_i), and through-Space P−P Distances (d) in the Me-DuPHOS− and UlluPHOS−(1,5-Cyclooctadiene)−Rhodium Complexes[a]

[(ligand)Rh(1,5-COD)]X	θ_1 (deg)[b] P−C−C(−P)	θ_2 (deg)[b] Rh−P−C_{ar}	θ_2 (deg) P−Rh−P	d (Å) P−P	l_1 (Å) (P−)C−C(−P)	l_2 (Å)[c] C_{ar}−P	l_3 (Å)[c] Rh−P	l_3 (Å)[d] Rh−C
(*S*,*S*)-Me-DuPHOS	117.2	110.25	84.72	3.056	1.400	1.812	2.268	2.244
(*R*,*R*)-UlluPHOS	117(3)	109.6(6)	85.86(2)	3.103(2)	1.437(3)	1.82(3)	2.278(2)	2.243(3)

[a] Average values are reported with rms and single values with esd (only for **4a**). [b] Average value of chemically equivalent angles. [c] Average value of the chemically equivalent bond lengths. [d] Average value of four chemically equivalent (1,5-cyclooctadiene)−Rh−carbon bond lengths.

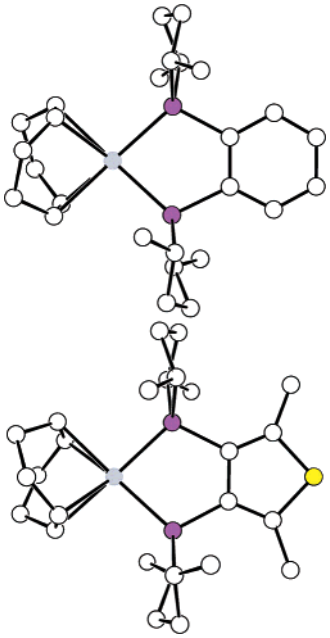


FIGURE 1. Projections on the plane of the aromatic rings of [[(*R*,*R*)-UlluPHOS]Rh(1,5-cyclooctadiene)] cation (**4a**) (bottom) and [[(*S*,*S*)-Me-DuPHOS]Rh(1,5-cyclooctadiene)SbF_6] cation (top); green = Rh, violet = P, yellow = S, black = C.

Since the geometry of chiral ligands is known to be a crucial parameter influencing the facial selection of their metal complexes, similar levels of absolute stereocontrol could be expected for the catalysts prepared from UlluPHOS and Me-DuPHOS.

It has been amply demonstrated that the electronic properties of chiral ligands can also greatly influence stereoselection in metal-based catalysis. We have previously assessed the electronic characteristics of a range of phosphine ligands through cyclic voltametric measurements.[1c,2] In a similar fashion, we have determined the electrochemical oxidation peak potential in order to assess the electronic availability at the phosphorus atoms of UlluPHOS. Voltammetric experiments showed that the oxidation peak of the new ligand occurred at 0.17 V, much lower than that exhibited by Me-DuPHOS ($E°_p$ = 0.36 V), indicating that the strategy adopted for producing a very electron-rich diphosphine was successful.[12] Some differences might be expected, therefore, in the kinetic behavior of the hydrogenation reactions of carbon−carbon and carbon−oxygen double bonds, which have been shown to be sensitive to the electronic availability of the donor functions of the ligand.

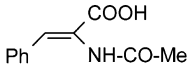
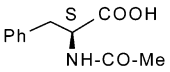
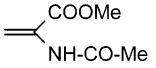
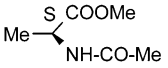
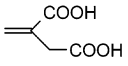
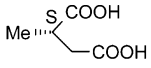
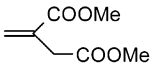
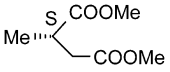
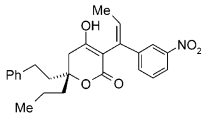
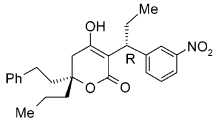
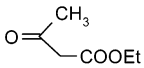
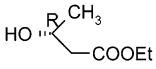
Hydrogenation precatalysts containing the Rh complexes of UlluPHOS and Me-DuPHOS were prepared in situ by reaction of the ligands with $[Rh(COD)_2]BF_4$ and applied in parallel reactions to assess the relative effectiveness of these catalysts for carbon−carbon double bond hydrogenation. Several typical substrates were screened, namely methyl 2-acetamidoacrylate, 2-acetamidocinnamic acid, itaconic acid, and the methyl ester of the latter. Also the industrially attractive diastereoselective hydrogenation of **5** to compound **6**, which is a key intermediate for the preparation of the HIV protease inhibitor PNU-140690,[13] was examined: diastereoselectivities up to 91% with [[(*R*,*R*)-UlluPHOS]Rh(1,5-cycloctadiene)OTf] (**4b**) were achieved.

Some experiments also were devoted to compare the efficiency of the complex [(UlluPHOS)Ru(iodo)(*p*-cymene)]iodide (**4c**) with the same type of complex of Me-DuPHOS in the hydrogenation of the ketonic carbonyl double bond of acetoacetic ester, even though the latter ligand is known not to be the ligand of choice for this kind of reaction, probably because the bite angle is too low in its metal complexes.[14]

(12) We determined the electrochemical oxidative potential of the 2,3-bis[(2*R*,5*R*)-2,5-dimethyl-phospholano]thianaphthene (Solvias Buti-PHOS), cited above, that we had prepared and tested with meager results in some of the test reactions of Table 2. The choice of electron-poor thianaphthene as a backbone for the phospholane rings has as a consequence a net decrease in the electronic richness of both the phosphorus atoms, in particular of the phospholane unit located in α position ($E°_p$ = 0.65 V).

(13) Fors, K. S.; Gage, J. R. *J. Org. Chem.* **1998**, *63*, 7348−7356.

TABLE 2. Comparative Data of Some Hydrogenation Reactions of Standard Substrates Promoted by (*R*,*R*)-UlluPHOS and (*R*,*R*)-Me-DuPHOS Metal Complexes

Entry	Substrate	Product	P_{H2} (psi)	Solvent	S/C	T (°C)	Time (m)	Conv.% UlluPHOS (MeDuPHOS)	ee% UlluPHOS (MeDuPHOS)
1			30	EtOH	1000	27	60	100 (100)	98.9[a] (95)[a]
2			40	MeOH	1000	27	60	100 (100)	>99.5 [b] (>99.5)[b]
3			30	MeOH	1000	40	340	77 (69.4)	48[c] (54)[c]
4			30	MeOH	1000	27	170	100 (100)	>99.5 [b] (>99.5)[b]
5	 **5**	 **6**	80	MeOH	1000	27	1200	100 (100)	91.0 (de)[d] (93.0) (de)[d]
6			1470	EtOH	1000	70	1440	33.6 (36)	58[a] (60)[a]

[a] Determined by chiral HPLC. [b] Evaluated by ^{1}H NMR spectroscopy with Eu(III)tris[3-(heptafluoropropylhydroxymethylene)-*d*-camphorate] as a shift reagent. [c] Evaluated by ^{1}H NMR spectroscopy on the methyl ester with Eu(III)tris[3-(heptafluoropropylhydroxymethylene)-*d*-camphorate] as a shift reagent. [d] Determined by HPLC.

The comparative stereoselection data are reported in Table 2 together with the main experimental parameters.

The analysis of the data reported in Table 2 indicates that the stereoselection levels observed in the reactions promoted by the complexes of UlluPHOS are fully comparable to those produced by the analogous Me-DuPHOS complexes, with the exception of itaconic acid, where the enantiomeric excess produced by the UlluPHOS rhodium complex was found to be somewhat lower than that attained with the Me-DuPHOS complex. This observation is in agreement with some recent literature data, demonstrating that the rhodium complexes of electron-rich diphosphines display an unexplained modest enantioselection ability for this specific substrate.[15]

As for the kinetic data, we were able to draw comparatively significant, even though not absolutely validated, values for the reaction rate constants.[16] In the case of the hydrogenation of 2-acetamidocinnamic acid, under identical experimental conditions (entry 1 of Table 2), we found rate constant values of 8.5×10^{-3} versus 1.1×10^{-3} depending whether the promoter was derived from UlluPHOS or Me-DuPHOS. In agreement with these findings, 94% conversion, reached by employing the UlluPHOS complex, was compared with 59% conversion, obtained with the Me-DuPHOS complex, after 0.5 h reaction time, and 99.5% versus 95.6% conversion after 1 h. Analogously, in the hydrogenation of itaconic acid promoted by the UlluPHOS complex, the conversion was found to be 26% after 1 h reaction time, while it was 12% when the Me-DuPHOS Rh complex was employed as mediator.

Conclusions

The conclusions that can be drawn from the results of this research are the following: (i) A new C_2 symmetric diphospholane ligand (**1**, UlluPHOS) containing a thiophene ring as the linker between the phospholane units was synthesized and structurally characterized. (ii) The synthesis of **1** (and steric homologues) is simpler than that available for the DuPHOS ligands family. (iii) The new ligand displays geometric properties (single-crystal

(14) Burk, M. J.; Harper, T. G. P., Kalberg, C. S. *J. Am. Chem. Soc.* **1995**, *117*, 4423−4424.

(15) Herseczki, Z.; Gergely, I.; Hegedüs, C.; Szöllösy, Bakos, J. *Tetrahedron: Asymmetry* **2004**, *15*, 1673−1676.

(16) Repetitive venting of the autoclave for sampling sometimes produces degradation of the catalyst with consequent rate depression.

X-ray analysis and theoretical calculations) very similar to those found for Me-DuPHOS but quite higher electronic availability at phosphorus ($E°_p$) relative to the latter ligand. (iv) The facial recognition and enantioselection associated with Rh and Ru complexes of UlluPHOS and Me-DuPHOS were shown to be similarly high in several typical test hydrogenation reactions. (v) Preliminary data suggest that olefin hydrogenation reactions promoted by catalysts bearing UlluPHOS are qualitatively faster than those using analogous catalysts of Me-DuPHOS. (vi) The promising results obtained with UlluPHOS suggest the extension of the hetero-DuPHOS family by applying this structural design to other electron-rich heterocycles, pyrrole in particular, for which the introduction of the phosphorus atoms could be even easier than that demonstrated in the case of thiophene.[7]

Experimental Section

Unless otherwise specified, all solvents and reagents were reagent grade and used without purification. ^{1}H NMR spectra were recorded as solutions in $CDCl_3$ on 200 or 300 MHz spectrometers. All reactions were performed using standard Schlenk-type techniques. For the preparations of the complexes and the hydrogenation reactions, solvents degassed under argon were employed. Hydrogenation reactions were carried out in a stirred (550 rpm), 100 mL, hastelloy autoclave, equipped with a sampling pipe extending to the bottom of the vessel.

Preparation of 2,5-Dimethyl-3,4-bis(diethoxyphosphoryl)thiophene (3). A solution of 2,5-dimethyl-3,4-diiodothiophene[10] (4.0 g) in triethyl phosphite (15 mL) was dropped under a N_2 atmosphere in 2 h into a stirred suspension of palladium acetate (0.98 g) in triethyl phosphite (20 mL) at 140 °C. The reaction was heated at 140 °C for further 3 h and then excess triethyl phosphite was removed in a vacuum. The oily residue was extracted with five 10-mL portions of heptane, and the combined extracts were evaporated to dryness to give an oil which was chromatographed (eluant, AcOEt/EtOH 9:1) to give **3** (1.4 g) as a colorless oil (48% yield). A sample was purified by distillation under reduced pressure (bp 170−175 °C at 3 Torr) to give **3** as a colorless, low-melting solid which was crystallized from pentane (mp 35 °C): ^{1}H NMR ($CDCl_3$) δ 1.78 (t, 12H, J = 53.6 Hz), 3.12 (d, 6H, J = 1.6 Hz), 4. 58 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 16.4 (t, J = 6.7 Hz), 53.7, 62.0 (d, J = 10.6 Hz), 124.9 (d, J = 18.8 Hz), 128.8 (d, J = 18.3 Hz), 150.4 (t, J = 4.8 Hz; ^{31}P NMR ($CDCl_3$) δ 12.5; PM (MS) 384. Anal. Calcd for $C_{14}H_{26}O_6P_2S$: C, 43.75; H, 6.82. Found: C, 43.55; H, 6.99.

Preparation of 2,5-Dimethyl-3,4-bis(phosphino)thiophene (2). Trimethylchlorosilane (11.2 mL) was added to a suspension of $LiAlH_4$ (3.6 g) in THF (80 mL), at −78 °C, under N_2, and the mixture was stirred at room temperature for 2 h. The solution was cooled to −60 °C and a solution of **3** (5.6 g) in dry THF (20 mL) was added. The reaction mixture was stirred at room temperature for 3 h and then water (3.6 mL), a 15% NaOH solution (3.6 mL), and water (10.8 mL) were added in sequence. The mixture was left stirring up to the formation of a precipitate, which was filtered off and washed with four 20-mL portions of THF. Removal of the solvent from the filtrate left a residue which was dissolved in toluene (50 mL) and washed twice with water (2 × 20 mL). The organic phase was filtered on Decalite and evaporated to dryness to give **2** as a pale-yellow oil (90% yield). A sample was purified by distillation under reduced pressure (bp 75 °C at 5 Torr) to give **2** as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 2.96 (6H, s), 3.67 (t, 2H), 4.70 (t, 2H); ^{13}C NMR ($CDCl_3$) δ 15.9 (t, J = 4.2 Hz), 127.2, 141.6 (t, J = 10.9 Hz); ^{31}P NMR ($CDCl_3$) δ −154.7 (t, J = 6 Hz); PM (MS) 176. Anal. Calcd for $C_6H_{10}P_2S$: C, 40.91; H, 5.72. Found: C, 40.66; H, 5.88.

Preparation of 2,5-Dimethyl-3,4-bis[(2*R*,5*R*)-2,5-dimethylphospholano]thiophene (1) (UlluPHOS). *n*-BuLi (0.79 mL of a 1.6 M solution in hexane) was added to a stirred solution of 2,5-dimethyl-3,4-bis(diphosphino)thiophene (**2**) (0.11 g) in THF (12 mL) at room temperature. The solution was left stirring for 1.5 h and then a THF solution (1.2 mL) of (2*S*,5*S*)-hexanediol cyclic sulfate (0.23 mg) was added. After 2 h of stirring, *n*-BuLi (0.87 mL of a 1.6 M solution in hexane) was added to the mixture at room temperature. The solution was stirred for 12 h and then MeOH (0.2 mL) was added. The solvent was removed under reduced pressure and the solid residue was treated with degassed CH_2Cl_2 and filtered under argon atmosphere, and the filtrate was evaporated to dryness to give a solid which was crystallized from MeOH to give **1** (0.19 g) in a pure state (70% yield): ^{1}H NMR ($CDCl_3$) δ 0.99 (6H, m), 1.15 (6H, m), 1.20−1.52 (4H, m), 1.94−2.2 (4H, m), 2.42 (6H + 2H, s superimposed to a m), 3.02 (2H, m); ^{13}C NMR ($CDCl_3$) δ 16.5, 18.6, 20.8 (t, J = 11.5 Hz), 29.6, 34.1 (t, J = 6.1 Hz), 36.1 (t, J = 3.4 Hz), 37.9, 136.6, 137.9; ^{31}P NMR ($CDCl_3$) δ 5.6 (s); $[\alpha]^{25}_D$ = + 54.2 (c = 1, $CHCl_3$); PM (MS) 444. Anal. Calcd for $C_{18}H_{26}P_2S$: C, 72.95; H, 5.90. Found: C, 73.11; H, 5.77.

Preparation of [(COD)Rh(UlluPHOS)]$^+$BF$_4^-$ (4a). A mixture of $[Rh(COD)_2]BF_4$ (9.7 mg) and **1** (9 mg) in degassed CH_2Cl_2 (1.5 mL) was stirred for 2 h. The solvent was evaporated under vacuum and the orange complex used without any purification: ^{31}P NMR ($CDCl_3$) 51.1 (d, J = 146 Hz).

Crystals of the complex suitable for X-ray analysis were obtained by stirring a solution of **1** (50 mg) and $[Rh(COD)_2]$-BF_4 (59 mg) in degassed CH_2Cl_2 (5 mL) for 2 h. THF (2.5 mL) and *n*-hexane (5 mL) were added and the solvents slowly evaporated until some crystals precipitated. After 24 h, the precipitation was complete, and the crystals were washed first with Et_2O and then with THF.

Preparation of [(COD)Rh(UlluPHOS)]$^+$OTf$^-$ (4b). A mixture of $[Rh(COD)_2]OTf$ (108.9 mg) and **1** (90 mg) in degassed CH_2Cl_2 (10 mL) was stirred for 2 h. The solvent was evaporated to one-third of its volume, and then THF (6 mL) and *n*-hexane (4 mL) were added. The solvent was evaporated under reduced pressure until crystallization started. The mixture was kept at −5 °C in a refrigerator and then the orange solid precipitate was collected, washed with *n*-hexane (3 × 4 mL), and dried under vacuum to give the complex (0.1 g): ^{31}P NMR ($CDCl_3$) 49.7 (d, J = 134 Hz).

Preparation of [(*p*-Cymene)Ru(UlluPHOS)I]I (4c). A solution of $[(RuI_2(p\text{-cymene})_2]$ (0.0014 mmol) and **1** (0.0035 mmol) in degassed CH_2Cl_2 (25 mL) and MeOH (9 mL) was refluxed for 2 h. The solvent was evaporated to dryness and the red complex used without any further purification: ^{31}P NMR ($CDCl_3$) δ 79. 25 (d, J = 45.5 Hz), 59.99 (d, J = 45.5 Hz); PM (ESI positive) 703.1.

X-ray Crystallography: [(COD)Rh(UlluPHOS)]$^+$BF$_4^-$ (4a). X-ray Structure Determination of the [((*S*,*S*)-Me-DuPHOS)Rh(1,5-cycloctadiene)]BF$_4$ Complex. Crystal data: $C_{26}H_{42}P_2RhS^+$ BF_4^-, 0.2965(C_4H_8O), 0.2035(CH_2Cl_2). fw = 677.04, monoclinic red crystal 0.32 × 0.21 × 0.11 mm^3, space group $C2$, a = 14.764(2) Å, b = 17.671(3) Å, c = 11.940(2) Å, β = 103.858(6)°, V = 3024.4(8) Å^3, Z = 4, ρ_{calc} = 1.486 g cm^{-3}, μ(Mo $K\alpha$) = 0.818 mm^{-1}, 20 633 reflections measured at 90 K, below θ = 33.05°, 10 291 unique [9047 with $I > 2\sigma(I)$], R(ave) = 0.248, 366 parameters refined on F^2 using SHELXL[17] code to final indices R(all) = 0.0401, wR =0.0836^{-3}, $\{w = 1/[\sigma^2(F^2)+(0.0495P)^2]$, where $P = (F_o^2 + 2F_c^2)/3\}$. The following are the refinement details: the tetrafluoroborate anion is disordered, but its interpretation and refinement were sufficiently easy and suitable. Much more difficult was understanding the nature of the solvent lying on the crystallographic 2-fold axis. Because the salt was crystallized from CH_2Cl_2, THF, and Et_2O,

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we attempted to introduce each one of the three pure solvent, time by time, in the refinement, with unsatisfactory results. The final refined model for the solvent was a mixture of CH_2Cl_2 and THF. Despite the large anisotropy and magnitude of atomic displacement parameters of the solvent (particularly for THF) and the correlations between the same, we adopted this model because it gave the lowest R and wR and the smallest residues in the solvent cavity, being nearly irrelevant with respect the remaining refinement parameters. The CCDC reference number is 264288.

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Supporting Information Available: Voltammetric curve for **1**; ESI spectra for complex **4c** with experimental and calculated isotopic distribution patterns; ^{1}H NMR spectra of complexes **4c** and **4a** and analogous Me-DuPHOS complexes; X-ray diffraction data for **4a**, including tables of positional and isotropic thermal parameters, anisotropic thermal parameters, interatomic bond distances, and intramolecular and torsion angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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