Synthesis of New Chiral Heterobimetallic Chromium−Ruthenium Complexes by Regioselective Insertion of Ruthenium into the C−S Bond of Tricarbonyl-η^6-[(thiophenyl)arene]chromium Complexes

José Giner Planas, Damien Prim,† Françoise Rose-Munch,* and Eric Rose

Laboratoire de Synthèse Organique et Organométallique, UMR CNRS 7611, Case Courrier 181, Université Pierre et Marie Curie, 4 Place Jussieu, 75252 Paris Cedex 05, France

René Thouvenot and Jacqueline Vaissermann

Laboratoire de Chimie Inorganique et Matériaux Moléculaires, UMR CNRS 7071, Case Courrier 42, Université Pierre et Marie Curie, 4 Place Jussieu, 75252 Paris Cedex 05, France

Received April 3, 2002

We report the synthesis of a series of chiral heterobimetallic complexes of the type Ru(SCR=CHCR′=CH)(depe)$_2$ [R = (η^6-arene)Cr(CO)$_3$, R′ = H or R = H, R′ = (η^6-arene)Cr(CO)$_3$] and one X-ray structure. All new complexes react with MeI, affording the analogous cationic complexes [Ru(S(Me)CR=CHCR′=CH)(depe)$_2$][I], and the diamagnetic NMR chiral shift reagent TRISPHAT anion has been used to differentiate the enantiomers of a selected complex in solution.

Thiophene binding modes and ring-opened intermediates of transition metal centers have been extensively studied as models for the homogeneous hydrodesulfurization (HDS) of petroleum feedstock in industry.[1] Since cleavage of the C−S bond by metal insertion is considered to be one of the key steps in HDS, a number of single metal[1,2] and homobimetallic[3] inserted thiophene complexes have been described. However, heterobimetallic inserted thiophenes are rare. They include a Mn−Pt complex obtained by insertion of Pt(PPh$_3$)$_3$ into the C−S bond of [(η^5-2,5-dimethylthiophene)Mn(CO)$_3$]$^+$ or those prepared by reaction of previously inserted Rh- or Ir-thiophene complexes with unsaturated M(CO)$_5$ fragments (M = Cr, Mo, W).[4,5]

Thiophenes react with coordinately unsaturated electron-rich metal complexes giving thiametallacycles. For example, it has been found[6] that the electron-rich "Ru(depe)$_2$" fragment regioselectively inserts into the C−S bond of thiophenes having electron-withdrawing substituents such as acyl or formyl groups. Whereas insertion into the 2-substituted thiophenes is controlled by steric effects, electronic effects seem to direct the insertion reaction of 3-substituted thiophenes as supported by semiempirical molecular orbital calculations.[6] In this paper we report the preparation of new chiral heterobimetallic Cr−Ru complexes as racemic mixtures of (Δ)- and (Λ)-isomers by complete regioselective insertion of the "Ru(depe)$_2$" fragment into the C−S bond of thiophenes bearing highly hindered and electron-withdrawing substituents such as tricarbonyl(arene)chro-

† Present address: Laboratoire SIRCOB, Bâtiment Lavoisier, Université Versailles-Saint-Quentin, 45 Avenue des Etats-Unis, 78035 Versailles Cedex, France.

(1) (a) Angelici, R. J. *Acc. Chem. Res.* **1988**, *21*, 387. (b) Angelici, R. J. *J. Coord. Chem. Rev.* **1990**, *105*, 61. (c) Rauchfuss, T. B. *Prog. Inorg. Chem.* **1991**, *39*, 259. (d) Sanchez-Delgado, R. A. *J. Mol. Catal.* **1994**, *86*, 287. (e) Angelici, R. J. In *Encyclopedia of Inorganic Chemistry*; King, R. B., Ed.; Wiley: New York, 1994; Vol. 3, pp 1433−1443. (f) Angelici, R. J. *Polyhedron* **1997**, *16*, 3073. (g) Bianchini, C.; Meli, A. *Acc. Chem. Res.* **1998**, *31*, 109. (h) Chen, J.; Angelici, R. J. *Coord. Chem. Rev.* **2000**, *206−207*, 63. (i) Angelici, R. J. *Organometallics* **2001**, *20*, 1259.

(2) (a) Jones, W. D.; Dong, L. *J. Am. Chem. Soc.* **1991**, *113*, 559. (b) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Frediani, P.; Herrera, V.; Sanchez-Delgado, R. A. *J. Am. Chem. Soc.* **1993**, *115*, 2371. (c) Garcia, J. J.; Maitlis, P. M. *J. Am. Chem. Soc.* **1993**, *115*, 12200. (d) Jones, W. D.; Chin, R. M.; Crane, T. W.; Baruch, D. M. *Organometallics* **1994**, *13*, 4448. (e) Bianchini, C.; Herrera, V.; Jimenez, M. V.; Laschi, F.; Meli, A.; Sanchez-Delgado, R. A.; Vizza, F.; Zanello, P. *Organometallics* **1995**, *14*, 4390. (f) Garcia, J. J.; Mann, B. E.; Adams, H.; Bailey, N. A.; Maitlis, P. M. *J. Am. Chem. Soc.* **1995**, *117*, 2179. (g) Bianchini, C.; Frediani, P.; Herrera, V.; Jimenez, M. V.; Meli, A.; Rincon, L.; Sanchez-Delgado, R. A.; Vizza, F. *J. Am. Chem. Soc.* **1995**, *117*, 4333. (h) Bianchini, C.; Jimenez, M. V.; Meli, A.; Vizza, F. *Organometallics* **1995**, *14*, 3196. (i) Chen, J.; Angelici, R. J. *Organometallics* **1999**, *18*, 5721. (j) Morikita, T.; Hirano M.; Sasaki, A.; Komiya, S. *Inorg. Chim. Acta* **1999**, *291*, 341. (k) Hernandez, M.; Miralrio, G.; Arevalo, A.; Bernes, S.; Garcia, J. J.; Lopez, C.; Maitlis, P. M.; del Rio, F. *Organometallics* **2001**, *20*, 4061.

(3) (a) King, R. B.; Stone, F. G. A. *J. Am. Chem. Soc.* **1960**, *82*, 4557. (b) Dettlaf, G.; Weiss, E. *J. Organomet. Chem.* **1976**, *108*, 213. (c) Hübener, P.; Weiss, E. *J. Organomet. Chem.* **1977**, *129*, 105. (d) Ogilvy, A. E.; Draganjac, M.; Rauchfuss, T. B.; Wilson, S. R. *Organometallics* **1988**, *7*, 1171. (e) Dullaghan, C. A.; Sun, S.; Carpenter, G. B.; Weldon, B.; Sweigart, D. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 212. (f) Dullaghan, C. A.; Zhang, X.; Walther, D.; Carpenter, G. B.; Sweigart, D. W.; Meng, Q. *Organometallics* **1997**, *16*, 5604. (g) Dullaghan, C. A.; Carpenter, G. B.; Sweigart, D.; Choi, D. S.; Lee, S. S.; Chung, Y. K. *Organometallics* **1997**, *16*, 5688. (h) Zhang, X.; Dullaghan, C. A.; Watson, E. J.; Carpenter, G. B.; Sweigart, D. *Organometallics* **1998**, *17*, 2067. (i) Zhang, X.; Dullaghan, C. A.; Carpenter, G. B.; Sweigart, D.; Meng, Q. *Chem. Commun.* **1998**, 93. (j) Vicic, D. A.; Jones W. D. *J. Am. Chem. Soc.* **1999**, *121*, 7606. (k) Reynolds, M. A.; Guzei, I. A.; Angelici, R. J. *Organometallics* **2001**, *20*, 1071.

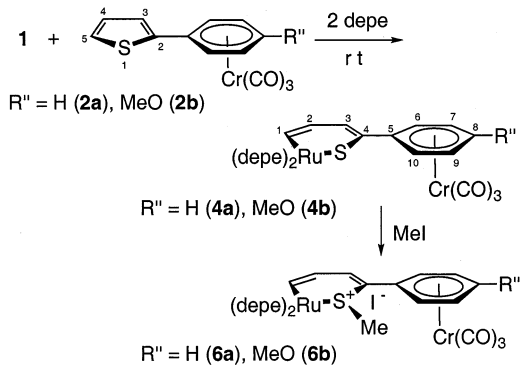
(4) Dullaghan, C. A.; Zhang, X.; Geene D. L.; Carpenter, G. B.; Sweigart, D. *Organometallics* **1998**, *17*, 3316.

(5) Bianchini, C.; Jiménez, M. V.; Meli, A.; Moneti, S.; Vizza, F. *Inorg. Chim. Acta* **1998**, *272*, 55.

(6) Giner-Planas, J.; Hirano, M.; Komiya, S. *J. Chem. Soc., Chem. Commun.* **1999**, 1793.

10.1021/om020264p CCC: $22.00
Publication on Web 09/18/2002

Scheme 1



mium complexes. We have also been able to differentiate both enantiomers of a selected cationic complex by using TRISPHAT as a diamagnetic NMR chiral shift reagent.

Reaction of Ru(COD)(COT) (**1**) (COD, 1,5-cyclooctadiene, COT, 1,3,5-cyclooctatriene) with the tricarbonyl-η^6-[(2-thiophenyl)arene]chromium (**2a**,**b**)[7] complexes in the presence of 2 equiv of depe [depe = 1,2-bis(diethylphosphino)ethane] in toluene at room temperature for 4 days afforded the new heterobimetallic complexes Ru(SCR=CHCH=CH)(depe)$_2$ [R = (η^6-benzene)Cr(CO)$_3$ (**4a**); R = (η^6-*p*-anisole)Cr(CO)$_3$ (**4b**)] as red solids in 54 and 45% yield, respectively (Scheme 1). The three noncoplanar chelate ligands (two depe and the inserted thiophene) induce chirality at Ru so that the complexes are obtained as a racemic mixture of (Δ)- and (Λ)-enantiomers.

The $^{31}P\{^1H\}$ NMR spectrum of complex **4a** displays an AMNX pattern at δ 54.1, 47.1, 43.3, and 30.5 for four different phosphorus nuclei, consistent with the asymmetric nature of the complex. ^1H NMR for this complex exhibits the typical resonances for a 1,5-inserted thiophene[6] at δ 7.96 (br t, J = 12.0 Hz, H_1), 7.45−7.23 (m, H_2), and 6.8 (d, J = 8.0 Hz, H_3). Homodecoupling experiments confirmed that protons H_1 and H_2 are mutually coupled and coupled with P nuclei, but H_3 displays coupling with H_2 only. A dtd resonance at δ 162.4 in the $^{13}C\{^1H\}$ NMR spectrum of **4a** for the thiaruthenacycle carbon atom C_1 attached to Ru also provides strong evidence for the formulation of the C−S insertion product. Two interesting features of the arene proton resonances must be underlined: (i) the *ortho*- and *meta*-protons are diastereotopic and (ii) the *ortho*-protons are strongly deshielded with respect to *meta*- and *para*-protons. For example, complex **4a** shows two different resonances for both *ortho*-protons at δ 6.41 (dd) and 6.18 (brd), but the *meta*- and *para*-protons appear as a broad signal at δ 4.6−4.5. Similarly all arene carbons are different (see Experimental Section). The diastereotopic nature of the arene protons and carbons in these complexes can be explained by the presence of the Cr(CO)$_3$ moiety. Its coordination to the unsymmetric arene ligand makes both *ortho*- and *meta*-protons become nonequivalents. The impressive downfield shift for the *ortho*-protons (about 1.8 ppm higher than the *meta*- and *para*-protons as confirmed by homodecoupling experiments) could be attributed to the conformation in solution of the Cr(CO)$_3$ tripod eclipsing *ortho*- and *para*-protons (*anti-eclipsed* with respect to the thiaruthenacycle; Supporting Information).[8] In addition, C−H···S interactions of the *ortho*-protons may also contribute to the deshielding and the difference in chemical shifts for these protons (vide infra).Complex **4a** crystallizes from benzene to afford deep red crystals suitable for X-ray structure analysis (Figure 1). The Cameron view of **4a** clearly shows that the "Ru(depe)$_2$" fragment is inserted into the C(5)−S bond of the 2-substituted thiophene. It is also important to note that the thiaruthenacycle ring is not coplanar with the arene ring in **4a** but displays a dihedral angle of 41°, the Cr(CO)$_3$ tripod being away from the phosphine ligand (P1−P2). The short distance between the *ortho*-proton attached to C-10 and sulfur [2.71(4) Å] indicates that there is likely an intermolecular interaction.[9] This interaction may explain the chemical shift differences between the two *ortho*-protons of the arene in **4a**,**b** in solution (670 and 230 ppb, respectively). Moreover, if we suppose that the dihedral angle between the arene and thiaruthenacycle is close to 90° in solution, this would allow interaction of both *ortho*-protons with the sulfur atom, explaining the large deshielding with respect to the *meta*-protons.

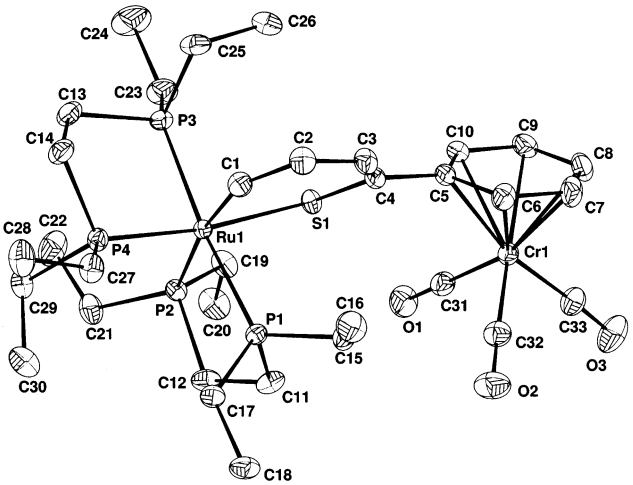


Figure 1. Cameron view of complex **4a**. Selected bond lengths (Å): Ru−C1 2.102(2), C1−C2 1.341(3), C2−C3 1.446(3), C3−C4 1.359(3), C4−C−S 1.738(2), Ru−S 2.4359-(5), C5−C6 1.420(3), C6−C7 1.413(4), C7−C8 1.392(5), C8−C9 1.409(4), C9−C10 1.406(3), C10−C5 1.412(3). Selected bond angles (deg): P1−Ru−P2 83.15(2), P1−Ru−P3 174.12-(2), P1−Ru−P4 100.98(2), S1−Ru−P1 85.74(2), P1−Ru−C1 89.83(6), P3−Ru−P4 84.02(2), P2−Ru−P4 99.28(2), P2−Ru−C1 171.42(6), S1−Ru−P4 172.35(2).

The spectroscopic data for **4b** are also consistent with a 1,5-inserted thiaruthenacyclic structure as depicted in Scheme 1.[10] In neither **4a** nor **4b** did we find evidence for "restricted" rotation of the Cr(CO)$_3$ group, which could also contribute to the nonequivalence of the

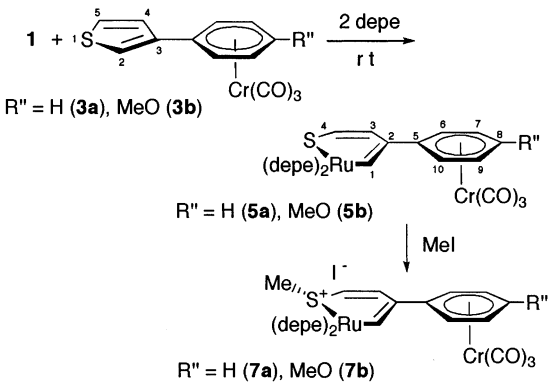
(7) We have recently improved the synthesis of these complexes. They are conveniently prepared by Stille cross-coupling reactions (Prim, D.; Tranchier, J.-P.; Rose-Munch, F.; Rose E.; Vaissermann, J. *Eur. J. Inorg. Chem.* **2000**, 901).

(8) It is known that although the conformers interconvert readily in solution, the preferred conformation is usually the same as in the solid state. See for example: (a) Abel, E. W.; Stone, F. G. A.; Wilkinson, G. *Comprehensive Organometallic Chemistry II*; 1994; Vol. 5, pp 497−501. (b) Rose-Munch, F.; Gagliardini, V.; Renard, C.; Rose, E. *Coord. Chem. Rev.* **1998**, *178*−*180*, 249. (c) Rose-Munch, F.; Rose, E. *Curr. Org. Chem.* **1999**, *3*, 445.

(9) Sun, W.-Y.; Shi, X.-F.; Zhang, L.; Hu, J.; Wei, J.-H. *J. Inorg. Biochem.* **1999**, *76*, 259.

(10) Experimental part for complexes **4b**, **5a**,**b**, **6a**,**b**, and **7a**,**b** are deposited as Supporting Information.

Scheme 2



carbons and protons of the arene ligand. Thus, both complexes show sharp singlets for the CO ligands in their $^{13}C\{^1H\}$ NMR spectra.

The regioselectivity of the insertion in **4a**,**b** is probably directed by steric factors as observed in other 2-substituted thiophenes.[2,3,6] The C(2)−S bond of the tricarbonyl-η^6-[(2-thiophenyl)arene]chromium (**2a**,**b**) is too congested so that the "Ru(depe)$_2$" fragment prefers to insert in the more accessible C(5)−S bond.

Heterobimetallic complexes Ru(SCH=CHCR=CH)(depe)$_2$ [R = (η^6-benzene)Cr(CO)$_3$ (**5a**), R = (η^6-*p*-anisole)Cr(CO)$_3$ (**5b**)] were also synthesized as racemic mixtures of Δ- and Λ-isomers by reaction of **1** with tricarbonyl-η^6-[(3-thiophenyl)arene]chromium (**3a**,**b**) and 2 molar equiv of depe as shown in Scheme 2.

Complex **5a** also displays an AMNX spin system in its $^{31}P\{^1H\}$ spectrum, consistent with the absence of a symmetry plane in the molecule (vide supra). The ^1H NMR of this complex displays the typical resonances for a 1,2-thiophene inserted thiaruthenacycle ring[6] at δ 8.18 (brd, J = 17.8 Hz, H_1), 6.67 (t, J = 10.0 Hz, H_3), and 6.37 (dd, J = 10.0, 2.0 Hz, H_4). As already observed in complex **4a**, the arene protons of **5a** are also diastereotopic due to the lack of symmetry of the complexes (see Supporting Information). NMR data for complex **5b** are also consistent with a 1,2-inserted product. It is important to note that, in this case, the differences of chemical shifts between *ortho*- and *meta*-protons is smaller than in the case of complexes **4a**,**b**. A difference of 0.65 and 1.01 ppm was found for complexes **5a** and **5b**, repectively. This is in agreement with a major *anti-eclipsed* conformation of the Cr(CO)$_3$ tripod with respect to the thiaruthenacycle.[8] However, the sulfur atom is far enough from the (η^6-benzene)Cr(CO)$_3$ ligand in **5a**,**b**, so that interaction between sulfur and *ortho*-protons is unlikely, explaining the smaller chemical shift differences with respect to **4a**,**b**.

In all cases, the exclusive 1,5- or 1,2-insertion was confirmed by NMR analysis of the reaction mixture prior to the isolation of solid samples. Residual starting tricarbonyl-η^6-[(thiophenyl)arene]chromium complexes were also observed in all cases, counting for the moderate yields in some complexes. Fortunately, different solubilities of starting and inserted complexes allowed us to separate them by precipitation or crystallization in most cases. Heating was avoided during the reactions to prevent decomplexation of the Cr(CO)$_3$ moiety.

Interestingly, the noncomplexed thiophenylarene ligands did not react with **1** and depe under the same reaction conditions. Therefore, the coordination of the Cr(CO)$_3$ moiety is strictly required to obtained the insertion products. This can be explained by "remote" activation of the C−S bonds by coordination of the Cr(CO)$_3$ moiety to the thiophenylarene ligands. Similar activation has been reported for thiophenes and dibenzothiophenes.[11] The present C−S insertion reaction can be interpreted by the mechanism reported by Harris and Jones.[12] In this mechanism, electron-withdrawing substituents in the thiophenes[13] are expected to stabilize the transition state, facilitating the insertion.[12] 1,2-Insertion of the "Ru(depe)$_2$" fragment into the C−S bond of tricarbonyl-η^6-[(3-thiophenyl)arene]chromium (**3a**,**b**) complexes is remarkable taking into account the bulkiness of the tricarbonyl(arene)chromium moiety. Although the same regioselectivity has been previously observed by Komiya et al., in their case the substituents were the small acyl or formyl groups. The regioselectivity can be explained by preferential attack of Ru into the C-2 of the 3-substituted thiophene due to a larger coefficient on this carbon in the LUMO[6] or by a three-center interaction intermediate (S−Ru−Cr) which directs the insertion to the most congested C−S bond.

Reactions of **4a**,**b** and **5a**,**b** with MeI in toluene or benzene for 12 h gave exclusively the S-methylated cationic adducts [Ru{S(Me)CR=CHCR′=CH}{depe}$_2$][I] [R = (η^6-benzene)Cr(CO)$_3$, R′ = H (**6a**); R = (η^6-*p*-anisole) Cr(CO)$_3$, R′ = H (**6b**); R = H, R′ = (η^6-benzene)-Cr(CO)$_3$ (**7a**); R = H, R′ = (η^6-*p*-anisole) Cr(CO)$_3$ (**7b**)], respectively, as yellow-orange solids insoluble in nonpolar solvents (Schemes 1 and 2).[10] NMR spectra for all cationic ruthenacycles resemble those of the starting compounds. In addition the SMe groups appear at δ 2.40−2.49 as doublets (J = 2.0−2.4 Hz) in their ^1H NMR spectrum, due to coupling with P atoms.[2h,i,6]

It is important to note that methylation at sulfur produces a significant effect on the *ortho*-protons so that they are less deshielded in **6a** than in **4a**. Since complex **6a** is "using" one of the sulfur lone pairs in the S−Me bond, it only has one left that may interact with the *ortho*-protons, and therefore the interaction would be weaker. This may indirectly explain the deshielding of the *ortho*-protons in these complexes (vide supra).

Enantiomer Differentiation by the TRISPHAT Anion. It has been recently shown that readily prepared and resolved tris(tetrachlorobenzenediolato)phosphate-(V) anion (TRISPHAT) is configurationally stable in solution as an alkylammonium salt, e.g., [*n*-Bu$_4$N][Δ-TRISPHAT].[14] This anion is a useful diamagnetic NMR chiral shift reagent for cationic transition metal complexes.[15]

(11) For example: (a) Zhang, X.; Yu, K.; Carpenter, G. B.; Sweigart, D. A.; Czech, P. T.; D'Acchioli, J. S. *Organometallics* **2000**, *19*, 1201. (b) Yu, K.; Li, H.; Watson, E. J.; Virkaitis, K. L.; Carpenter, G. B.; Sweigart, D. A. *Organometallics* **2001**, *20*, 3550. (c) Li, H.; Yu, K.; Watson, E. J.; Virkaitis, K. L.; D'Acchioli, J. S.; Carpenter, G. B.; Sweigart, D. A. *Organometallics* **2002**, *21*, 1262.

(12) Thiophene coordination to the metal through the S atom, followed by attack of the metal on the adjacent carbon atom via donation into the C−S antibonding orbital: (a) Harris, S.; Chianelli, R. R. *J. Catal.* **1984**, *86*, 400. (b) Dong, L.; Duckett, S. B.; Ohman, K. F.; Jones, W. D. *J. Am. Chem. Soc.* **1992**, *114*, 151.

(13) The electron-withdrawing character of the Cr(CO)$_3$ fragment is similar to that of the NO$_2$ group in benzere (refs 8b,c).

(14) (a) Lacour, J.; Gingliner, C.; Grivet, C.; Bernardinelli, G. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 608. (b) Lacour, J.; Gingliner, C.; Favarger, F. *Tetrahedron Lett.* **1998**, *39*, 4825.

Table 1. Significant Differences of Chemical Shift ($\Delta\delta$,[a] ^{1}H and ^{31}P{^{1}H} NMR, 300 MHz, CD_2Cl_2) for Protons and Phosphorus of 6a after Addition of TRISPHAT

	$\Delta\delta$ in ^{1}H NMR		$\Delta\delta$ in ^{31}P{^{1}H} NMR			
equiv of Trisphat	*ortho*-H(6 or 10)	SMe	P_A	P_M	P_N	P_X
0.83	20	19	32	0	42	0
1.61	30	24	41	0	55	0
2.91	40	30	55	18	80	0

[a] In ppb.

We selected complex **6a** for testing the TRISPHAT anion efficiency because most proton resonances are clearly separated in this complex and, as in complex **4a**, the *ortho*-protons resonate at lower field than the *meta*- and *para*-protons. Thus, small portions of [*n*-Bu_4N][Δ-TRISPHAT] were successively added to a CD_2Cl_2 solution of **6a**, and the formation of diastereomeric pairs was followed by ^{1}H and ^{31}P{^{1}H} NMR at room temperature. Separation of the NMR spectra for both enantiomers of the cationic complex was clearly observed after addition of 2.9 equiv of the chiral shift reagent (Table 1). Actually the *ortho*-proton at δ 5.90 splits into two doublets at δ 5.89 and 5.85. Whereas the other *ortho*-proton is apparently not affected by the addition of TRISPHAT, the doublet assigned to SMe at δ 2.36 is nicely split into two different resonances at δ 2.35 and 2.32. The *meta*- and *para*-protons are also affected by the addition of TRISPHAT, but partial overlapping between them prevents a clear analysis. Concerning the thiaruthenacyclic protons, it is difficult to detect any effect because of the broadening and complexity of these signals. In addition, a splitting of some resonances of the AMNX spin system is observed in the ^{31}P{^{1}H} NMR spectrum for **6a**, after addition of TRISPHAT. It is interesting to note that resonances at δ 55.2 (P_A) and δ 42.8 (P_N) are already split after addition of 0.83 equiv of the chiral anion, but the resonance at δ 47.7 (P_M) requires addition of 2.9 equiv and that at δ 29.9 (P_X) is not affected. These data suggest that the Δ-TRISPHAT anion approaches preferentially from one side of complex **6a** so that one of the diphosphine ligands (P_A and P_M) is more affected. Another interesting feature is also revealed by the ^{13}C-{^{1}H} NMR spectrum of **6a** after addition of 2.9 equiv of TRISPHAT. The spectrum shows a significant split (50−110 ppb) of four benzyl resonances and the CO signal, but no split of the thiaruthenacycle carbons is observed.

In summary, new chiral heterobimetallic complexes were obtained as racemic mixtures by completely regioselective 1,5- or 1,2-C−S bond insertion of the "Ru(depe)$_2$" fragment into the thiophene ring of tricarbonyl-η^6-[(2-thiophenyl)arene]chromium or tricarbonyl-η^6-[(3-thiophenyl)arene]chromium complexes, respectively. Regioselective 1,2-insertion into the thiophene of the bulky tricarbonyl-η^6-[(3-thiophenyl)arene]chromium complexes is remarkable and is probably achieved due to the electronic control exerted by the electron-withdrawing $Cr(CO)_3$ moiety. Thus, the present work clearly shows how selection of the appropiate substituent on thiophenes may induce Ru insertion reactions that otherwise do not take place, opening a new and general synthetic route to bimetallic complexes. In addition, the Δ-enantiomer of **6a** has been nicely differentiated from the Λ-enantiomer by using the diamagnetic chiral shift reagent TRISPHAT.

Experimental Section

General Procedures. All reactions and manipulations were routinely performed under a dry nitrogen atmosphere using Schlenk tube techniques. Benzene, hexane, and toluene were dried over sodium benzophenone ketyl, distilled, and stored in gastight solvent bulbs. The starting materials were prepared by the literature methods: Ru(COD)(COT),[16] tricarbonyl(Cl-benzene)chromium,[17] tricarbonyl(4-Cl-anisole)chromium,[17] tricarbonyl-η^6-[(2-thiophenyl)arene]chromium (**2a**,**b**),[7] and 2-thiophenyl-4-anisole.[7] Other reactants listed in the text were purchased from Strem Chemicals, Inc. and used as received. Infrared spectra were measured on a Perkin-Elmer 1420 spectrometer. ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectra were obtained on a Bruker AC200, AC300, or DRX500 spectrometer. The NMR differentiation experiments using TRISPHAT anion were run on the AC300 spectrometer equipped with a QNP probehead allowing ^{1}H, ^{31}P{^{1}H}, and ^{13}C-{^{1}H} NMR observation on the same sample. Elemental analyses were performed by Le Service de Microanalyses de l'Université Pierre et Marie Curie.

General Procedure for the Preparation of Ru(SCR=CHCH=CH)(depe)$_2$ [R = (η^6-benzene)Cr(CO)$_3$ (4a)]. Depe (160 μL, 0.672 mmol) and tricarbonyl-η^6-[(2-thiophenyl)benzene]chromium (**2a**) (99.6 mg, 0.334 mmol) were added to a solution of Ru(COD)(COT) (**1**) (105 mg, 0.333 mmol) in 5 mL of toluene. The reaction mixture was stirred at room temperature for 4 days, giving a deep red solution. After volatile materials were removed, the residual red oil was washed with hexane, giving a red precipitate that was dried under vacuum to yield pure **4a** (135 mg, 0.167 mmol): 50% yield. Anal. Calcd for $C_{33}H_{56}P_4O_3SRuCr$: C, 48.94; H, 6.97. Found: C, 48.96; H, 7.09. IR (benzene, cm^{-1}): 1950 (CO), 1870 (CO). ^{1}H NMR (200 MHz, benzene-d_6): δ 7.96 (brt, J = 12.0 Hz, 1H, H_1), 7.45−7.23 (m, 1H, H_2), 6.80 (d, J = 8.0 Hz, 1H, H_3), 6.41 (dd, J = 5.2, 3.0 Hz, 1H, H_6 or H_{10}), 6.18 (brd, J = 4.0 Hz, 1H, H_{10} or H_6), 4.6−4.5 (m, 3H, H_{7-9}), 2.6−0.6 (m, 48H, 2 *depe*). ^{31}P{^{1}H} NMR (121.5 MHz, benzene-d_6): AMNX spin system, δ 54.1 (ddd, J = 22.6, 19.8, 14.2 Hz, 1P, *eq*-P *trans* to sulfur), 47.1 (dt, J = 370.3, 19.8 Hz, 1P, *ap*-P), 43.3 (ddd, J = 370.3, 22.8, 13.9 Hz, 1P, *ap*-P), 30.5 (dt, J = 18.2, 13.4 Hz, 1P, *eq*-P *trans* to carbon). Selected ^{13}C{^{1}H} NMR (125.8 MHz, benzene-d_6): δ 235.6 (s, *C*O), 162.4 (dtd, 57, 15, 11 Hz, C_1), 130.6 (s, C_2), 124.2 (s, C_3), 94.8 (s, C_6 or C_{10}), 94.0 (s, C_{10} or C_6), 93.0, 92.7, 90.8, 90.7 (arene carbons).

Crystallographic Study of 4a. Intensity data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer using Mo Kα radiation. Accurate cell dimensions and orientation matrixes were obtained from least-squares refinements of the setting angles of 25 well-defined reflections. No significant decay in the intensity of two standard reflections was observed during the course of the data collections. Crystal data, collection parameters, and other significant details are listed in the Supporting Information.

The usual corrections for Lorentz and polarization effects were applied. Computations were performed by using CRYS-

(15) (a) Lacour, J.; Ginglinger, C.; Favarger, F.; Torche-Haldimann, S. *Chem. Commun.* **1997**, 2285. (b) Monchaud, D.; Lacour, J.; Coudret, C.; Fraysse, S. *J. Organomet. Chem.* **2001**, *624*, 388. (c) Amouri, H.; Thouvenot. R.; Gruselle, M.; Malézieux, B.; Vaissermann. *Organometallics* **2001**, *20*, 1904. (d) Giner-Planas, J.; Prim, D.; Rose, E.; Rose-Munch F.; Monchaud, D.; Lacour, J. *Organometallics* **2001**, *20*, 4107.

(16) (a) Pertici, P.; Vitulli, G. *J. Chem. Soc., Dalton Trans.* **1979**, 1961. (b) Itoh, K.; Nagashima, H.; Ohshima; T.; Oshima, N.; Nishiyama, H. *J. Organomet. Chem.* **1984**, *272*, 179.

(17) Mahaffy, C. A. L.; Pauson, P. L. *Inorg. Synth.* **1990**, *28*, 136.

TALS.[18] Scattering factors and corrections for anomalous dispersion were taken from *International Tables for X-ray Crystallography*.[19] The structures were resolved by direct methods (SIR92[20]) and refined by least squares with anisotropic thermal parameters for all nonhydrogen atoms. Hydrogen atoms were located on a Fourier difference map, and their coordinates were refined as well as an overall isotropic thermal parameter.

(18) Watkin, D. J.; Prout, C. K.; Carruthers, J. R.; Betteridge, P. W. *Crystals*, issue 10; Chemical Crystallography Laboratory: University of Oxford, U.K., 1996.

(19) Cromer, D. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV.

(20) Altomare, A.; Cascarano, G.; Giacovazzo G.; Guagliardi A.; Burla M. C.; Polidori, G.; Camalli, M. SIR92−a program for automatic solution of crystal structures by direct methods. *J. Appl. Crystallogr.* **1994**, (27), 435.

Acknowledgment. We thank the European Community (TMR program No. FMRX-CT98-0166 and COST D14 program) and CNRS for financial support. We also thank J. Lacour for the gift of resolved [cinchonidinium]-[Δ-TRISPHAT] and J. A. Gladysz for letting us prepare complex **4a** in his laboratory. J.G.P. thanks the TMR for a grant.

Supporting Information Available: General procedure for preparation of complexes **4b**, **5a**,**b**, **6a**,**b**, and **7a**,**b**. Two Cameron views of **4a**, tables of crystallographic data, atom coordinates, thermal parameters, and bond lengths and angles. ^{1}H NMR of **4a** in the absence and presence of TRISPHAT. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020264P