Regioselective 1,2-insertion of Ru into the C–S bond in 3-substituted thiophenes

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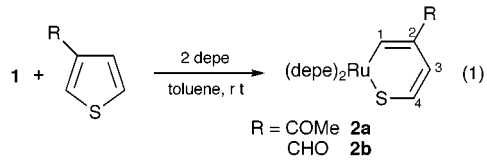
Reactions of [Ru(cod)(cot)] 1 [cod = cycloocta-1,5-diene, cot = cycloocta-1,3,5-triene] with 3-acetyl(or formyl)thiophene and 2-acetyl(or formyl) thiophene in the presence of depe [1,2-bis(diethylphosphino)ethane] lead to completely regioselective 1,2- or 1,5-insertion into the C–S bond giving the new thiaruthenacycles [Ru(SCR=CHCR′=CH)(depe)$_2$] [R = H, R′ = COMe (2a); R = H, R′ = CHO (2b); R = COMe, R′ = H (3a); R = CHO, R′ = H (3b)], respectively.

The study of coordination and reactivity of transition metal complexes with thiophene derivatives[1] is an area of increasing interest with regard to the hydrodesulfurization (HDS) reaction of fossil fuels.[2] In this sense, electron-withdrawing substituents at the 2- or 3-position of thiophene were reported to facilitate the insertion of Rh into the less congested C–S bond.[3] In addition, when small metal fragments were used, mixtures of the 1,2- and 1,5-insertion products were generally obtained.[4] We wish to report here the completely regioselective 1,2- or 1,5-insertion reactions of [Ru(cod)(cot)] **1** with thiophenes having an electron-withdrawing substituent at the 3- or 2-position, respectively, in the presence of depe.

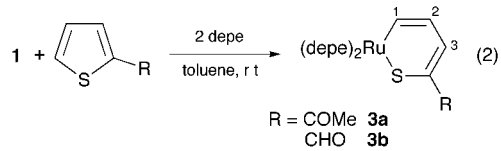
3-Acetylthiophene reacted with **1** in the presence of 2 equiv. of depe in toluene at room temperature for 12 h to give [Ru{SCH=CHC(COMe)=CH}(depe)$_2$] **2a**[5] in 72% yield, as a yellow solid [eqn. (1)].



The ^{31}P{^{1}H} NMR spectrum of **2a** shows an AMNX spin system at δ 54.8, 48.5, 45.5 and 28.8 for four different phosphorous nuclei, and the ^{1}H NMR spectrum exhibits resonances for the thiaruthenacycle protons at δ 10.73 (H^1), 6.61 (H^3) and 5.90 (H^4). 3-Formylthiophene reacted in a similar way giving [Ru{SCH=CHC(CHO)=CH}(depe)$_2$] **2b** in 68% yield [eqn. (1)]. The molecular structure of **2b** was established by X-ray structure analysis (Fig. 1).[6] The ORTEP drawing clearly shows that ring cleavage occurred at the C–S bond close to the substituent in spite of the steric repulsion. The six-membered ring defined by Ru, S, C1, C2, C3 and C4 atoms is basically planar, with no atom deviating by more than 0.1 Å from their mean plane. Furthermore, the C–C distances for C1–C2, C2–C3 and C3–C4 of 1.371(9), 1.44(1) and 1.33(1), respectively, indicate bond alternation suggesting a localized diene structure.

It is remarkable that the regioselective 1,2-insertion of the very bulky Ru(depe)$_2$ fragment takes place into the C–S bond of the 3-substituted thiophene, suggesting that the electronic effect is the major controlling factor in the selectivity of the insertion.

In contrast to the above results, **1** reacted with 2-acetylthiophene to give the 1,5-insertion product [Ru{SC(COMe)=CHCH=CH}(depe)$_2$] **3a**[7] in 84% yield, as a red solid (eqn. 2).



The ^{1}H NMR of **3a** shows resonances for the thiaruthenacycle protons at δ 8.36 (H^1), 7.98 (H^3) and 7.39 (H^2). Detailed analysis of coupling constants by homo-decoupling techniques indicated that protons H^1 and H^2 are coupled with the P nuclei (J_{H^1P} 18.0, 3.3 Hz and J_{H^2P} 12.3, 3.0 Hz) and between them ($J_{H^1H^2}$ 12.0 Hz), but H^3 only displays coupling with H^2 ($J_{H^2H^3}$ 7.5 Hz). A dtd resonance at δ 169.6 for C^1 in the ^{13}C{^{1}H} NMR spectrum of **3a** provides strong evidence for the formulation of the C–S insertion product. In addition, spectroscopic data of **3a** are comparable with those for the known thiaferracycle [Fe{SC(COMe)=CHCH=CH}(depe)$_2$] in which insertion also takes place into the C^5–S bond,[8] away from the substituent at the 2-position. 2-Formylthiophene reacted giving also the 1,5-insertion product [Ru{SC(CHO)=CHCH=CH}(depe)$_2$] **3b** in 36% yield [eqn. (2)]. Thus, the steric effect seems to be predominant in 2-substituted thiophenes. It is noteworthy that neither 2,5-dimethyl-3-acetylthiophene nor alkyl-substituted thiophenes reacted under the same reaction conditions.[9]

Reactions of **2a**, **b** and **3a** with MeI followed by treatment with NaBPh$_4$ gave exclusively the S-methylated cationic adducts [Ru(SCH$_3$CR=CHCR′=CH)(depe)$_2$][BPh$_4$] [R = H, R′ = COMe (**4a**); R = H, R′ = CHO (**4b**); R = COMe, R′ = H (**5a**)].[10] The molecular structure of **5a** has been unequivocally

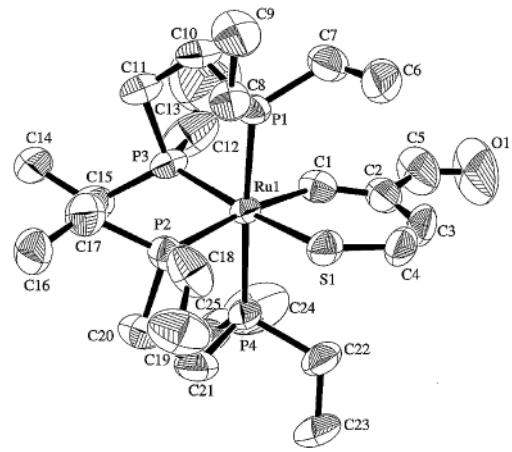


Fig. 1 An ORTEP drawing of **2b** with the numbering scheme. The hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Ru1–C1, 2.049(6), Ru1–S1 2.427(2), C1–C2 1.371(9), C2–C3 1.44(1), C3–C4 1.33(1), C4–S1 1.715(8); S1–Ru1–C1 90.3(2), Ru1–S1–C4 110.4(3), S1–C4–C3 130.9(6), C4–C3–C2 127.4(7), C3–C2–C1 126.9(7), C2–C1–Ru1 133.4(5).

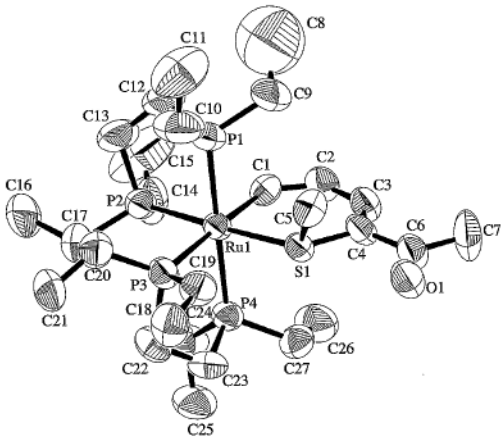


Fig. 2 An ORTEP drawing of **5a** with the numbering scheme. The tetraphenylborate anion and hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Ru1–C1, 2.044(9), Ru1–S1 2.423(2), C1–C2 1.38(1), C2–C3 1.44(1), C3–C4, 1.37(1) C4–S1 1.739(9); S1–Ru1–C1 89.3(2), Ru1–S1–C4 115.0(3), S1–C4–C3 124.6(7), C4–C3–C2 128.9(9), C3–C2–C1 129.1(8), C2–C1–Ru1 132.8(6).

determined by single-crystal X-ray structure analysis (Fig. 2).[6]

The ORTEP drawing of **5a** also supports that 1,5-insertion takes place in the 2-substituted thiophene. The thiaruthenacycle ring in **5a** is also planar (highest deviation from the best mean plane is 0.07 Å) with a localized diene structure of the C1–C2–C3–C4 linkage.

In all cases, except for **3b**, the formation of the thiaruthenacycles was very clean and no other side-products were observed when the reactions were followed by ^{1}H and ^{31}P{^{1}H} NMR.

The present Ru-promoted C–S bond cleavage of thiophenes may be essentially interpreted by the mechanism reported by Harris and Jones.[11] Thus, thiophene coordinates to the metal through the sulfur atom, followed by attack of the metal on the adjacent carbon atom *via* donation into the C–S antibonding orbital. As previously reported for a Rh complex,[3] electron-withdrawing substituents on the thiophene facilitate the C–S bond cleavage and, in fact, that is what we observed for Ru since alkylthiophenes did not react in our system. The preferred insertion of Ru into the C–S bond close to the substitutents in **2a** and **2b** can be interpreted in terms of the large coefficient on C^2 in the LUMO of these thiophenes bearing electron-withdrawing substituents.[12]

In conclusion, for the first time, electronic effects were found to be predominant in 3-substituted thiophenes leading exclusively to 1,2-insertion of Ru into the C–S bond, whereas steric effects become much more important in 2-substituted thiophenes affording only 1,5-insertion products.

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Notes and references

1 W. D. Jones, D. A. Vicic, R. M. Chin, J. H. Roache and A. W. Myers, *Polyhedron*, 1997, **16**, 3115; R. J. Angelici, *Polyhedron*, 1997, **16**, 3073; C. Bianchini and A. Meli, *Acc. Chem. Res.*, 1998, **31**, 109; C. Bianchini, D. Masi, A. Meli, M. Peruzzini, F. Vizza and F. Zanobini, *Organometallics*, 1998, **17**, 2495.

2 H. Topsoe, B. S. Clausen and F. E. Massoth, *Hydrotreating Catalysis*, Springer-Verlag, Berlin, 1996; R. R. Chianelli, M. Daage and M. J. Ledoux, *Adv. Catal.*, 1994, **40**, 177.

3 C. Bianchini, M. V. Jimenez, A. Meli and F. Vizza, *Organometallics*, 1995, **14**, 3196.

4 L. Dong, S. B. Duckett, K. F. Ohman and W. D. Jones, *J. Am. Chem. Soc.*, 1992, **114**, 151; W. D. Jones and L. Dong, *J. Am. Chem. Soc.*, 1991, **113**, 559; I. E. Buys, L. D. Field, T. W. Hambley and A. E. D. McQueen, *J. Chem. Soc., Chem. Commun.*, 1994, 557.

5 As a typical example, spectroscopic and analytical data of **2a**: Found: C, 48.33; H, 8.64; S, 5.09. Calc. for $C_{26}H_{54}OP_4RuS$: C, 48.81; H, 8.51; S, 5.01%. ^{1}H NMR (300 MHz, CD_3OD): δ 10.73 (br d, $^3J_{HP}$ 18.0 Hz, 1 H, H^1), 6.61 (dd, $^3J_{HH}$ 10.0, $^4J_{HH}$ 1.8 Hz, 1H, H^3), 5.90 (t, $^3J_{HH}$ 10.0, $^4J_{HP}$ 10.0 Hz, 1H, H^4), 2.25 (s, 3H, $COCH_3$), 2.2–0.8 (m, 48H, 2 depe). ^{31}P{^{1}H} NMR (121 MHz, CD_3OD), AMNX spin system: δ 54.8 (td, J 20.0, 16.0 Hz, 1P, eq-P *trans* to S), 48.5 (dt, J 329.4, 20.0 Hz, 1P, ap-P), 45.5 (ddd, J 329.4, 22.0, 17.0 Hz, 1P, ap-P), 28.8 (dt, J 20.0, 16.0 Hz, 1P, eq-P *trans* to C). Selected ^{13}C{^{1}H} NMR (75.5 MHz, CD_3OD): δ 200.8 (dtd, $^2J_{CP}$ 57.3, 15.0, 8.0 Hz, C^1), 196.1 (d, $^3J_{CP}$ 8.3 Hz, C^4). IR(KBr, cm^{-1}): 1615 ($\nu_{C=O}$).

6 *Crystal data*: for $C_{26}H_{52}OP_4RuS$ **2b**: M = 625.71, *monoclinic*, space group $P2_1/n$ (no. 14), a = 10.638(5), b = 15.753(5), c = 18.502(4) Å, β = 99.22(2)°, V = 3060(1) Å^3, T = 293 K, Z = 4, μ(Mo-Kα) = 8.06 cm^{-1}, $R(R_w)$ = 0.043(0.045) for 3792 reflections. For $C_{51}H_{77}OP_4RuSB$ **5a**: M = 974.0, monoclinic, space group $P2_1/c$ (no. 14), a = 11.485(5), b = 24.678(5), c = 18.369(4) Å, β = 95.22(3)°, V = 5184(2) Å^3, T = 293 K, Z = 4, μ(Mo-Kα) = 5.00 cm^{-1}, $R(R_w)$ = 0.068(0.081) for 6755 reflections. Single crystals of both **2b** and **5a** were recrystallised from acetone and mounted in a glass capillary. Both structures were solved using heavy atom Patterson methods and refined by full-matrix least squares on F. CCDC 182/1364. See http://www.rsc.org/suppdata/cc/1999/1793/ for crystallographic data in .cif format.

7 As a typical example, spectroscopic and analytical data of **3a**: Found: C, 48.10; H, 9.24; S, 4.85. Calc. for $C_{26}H_{54}OP_4RuS$: C, 48.81; H, 8.51; S, 5.01%. ^{1}H NMR (300 MHz, C_6D_6): δ 8.36 (ddq $^3J_{HP}$ 18.0, 3.0, $^3J_{HH}$ 12.0 Hz, 1H, H^1), 7.98 (d, $^3J_{HH}$ 7 Hz, 1H, H^3), 7.39 (tdt, $^4J_{HP}$ 12.3, 3.0, $^3J_{HH}$ 7.5 Hz, 1H, H_2), 2.86 (s, 3H, $COCH_3$), 2.5–0.5 (m, 48H, 2depe). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6), AMNX spin system: δ 53.6 (td, J 20.7, 13.8 Hz, 1P, eq- *trans* to S), 46.7 (dt, J 371.4, 21.0 Hz, 1P, ap-P), 43.3 (ddd, J 371.4, 19.1, 15.2 Hz, 1P, ap-P), 30.3 (dt, J 17.0, 15.0 Hz, 1P, eq-P *trans* to C). Selected ^{13}C {^{1}H} NMR (75.5 MHz, C_6D_6): δ 199.2 (d, $^3J_{CP}$ 7.5 Hz, C^4), 169.6 (dtd, $^2J_{CP}$ 57.3, 16.8, 9.8 Hz, C^1). IR(KBr, cm^{-1}): 1636 ($\nu_{C=O}$).

8 T. Morikita, M. Hirano, A. Sasaki and S. Komiya, *Inorg. Chim. Acta*, 1999, **291**, 341.

9 Thiophenes investigated: 2-methyl-, 3-methyl- and 2,5-dimethylthiophene.

10 As a typical example, selected spectroscopic and analytical data of **5a**: Found: C, 62.52; H, 8.00; S, 3.85. Calc. for $C_{51}H_{77}BOP_4RuS$: C, 62.89; H, 7.97; S, 3.29%. ^{1}H NMR (300 MHz, acetone-d_6): δ 9.78 (ddq, $^3J_{HP}$ = 16.0, 4.6, $^3J_{HH}$ 12.0 Hz, 1H, H^1), 7.88 (d, $^3J_{HH}$ 7.8 Hz, 1H, H^3), 7.00–6.90 (m, 1H, H^2), 2.45 (d, J 2.4 Hz, 3H, SCH_3), 2.37 (s, 3H, $COCH_3$). ^{31}P{^{1}H} NMR (121 MHz, acetone-d_6), AMNX spin system: δ 54.5 (ddd, J 29.0, 19.4, 16.5 Hz, 1P, eq-P *trans* to S), 48.1 (dt, J 244.3, 19.4 Hz, 1P, ap-P), 44.3 (ddd, J 244.3, 29.0, 14.6 Hz, 1P, ap-P), 29.5 (ddd, J 19.4, 17.0, 14.6 Hz, 1P, eq-P *trans* to C). IR(KBr, cm^{-1}): 1643 ($\nu_{C=O}$). Molar electric conductivity in acetone: Λ = 7.99 S cm^2 mol^{-1}.

11 (*a*) S. Harris and R. R. Chianelli, *J. Catal.*, 1984, **86**, 400; (*b*) L. Dong, S. B. Duckett, K. F. Ohman and W. D. Jones, *J. Am. Chem. Soc.*, 1992, **114**, 151.

12 Preliminary semiempirical calculations were carried out on 3-acetyl- and 3-formyl-thiophene using the MOPAC program in the Cache calculation package. Coefficients for C^2 and C^5 were −0.62 and −0.40 for 3-acetyl thiophene and −0.63 and −0.41 for 3-formyl thiophene, respectively.

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