

Thiophene C–S Bond Cleavage by Rhodium and Iridium. An Unprecedented Bridging Mode of the Open C₄H₄S Fragment

Alessia Bacchi,^c Claudio Bianchini,^{*a} Verónica Herrera,^b M. Victoria Jiménez,^a Carlo Mealli,^a Andrea Meli,^a Simonetta Moneti,^a Maurizio Peruzzini,^a Roberto A. Sánchez-Delgado^b and Francesco Vizza^a

^a Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione del CNR, Via J. Nardi 39, 50132 Firenze, Italy

^b Instituto Venezolano de Investigaciones Científicas, IVIC, Caracas 1020-A, Venezuela

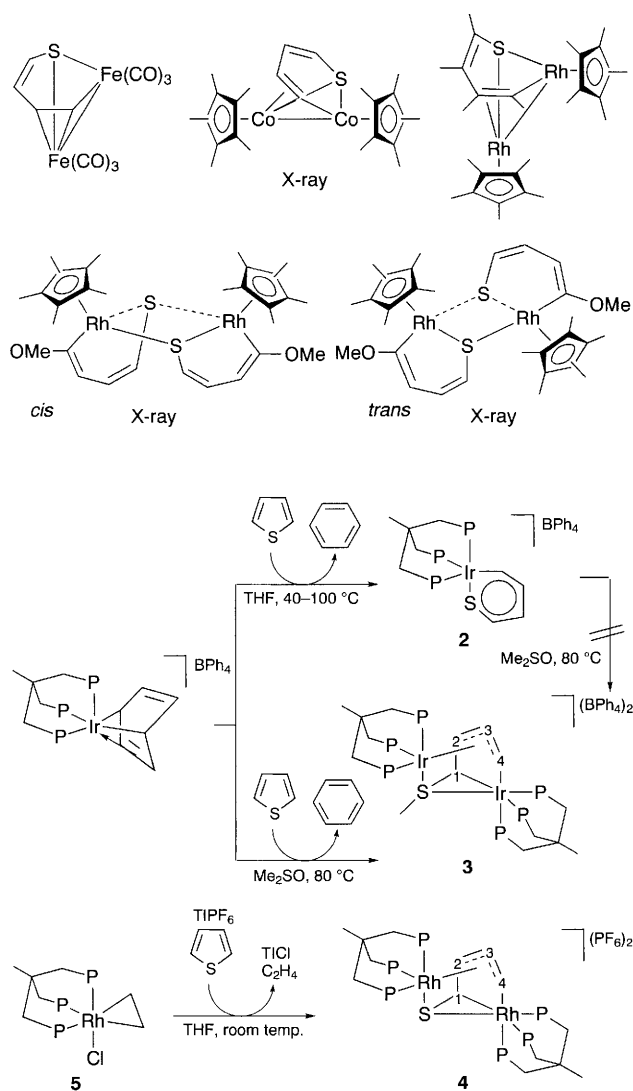
^c Dipartimento di Chimica Generale e Inorganica, Chimica Analitica, Chimica Fisica, Università di Parma, Viale delle Scienze, 43100, Parma, Italy

The complexes $[(\text{triphos})\text{M}]_2(\mu\text{-}\eta^3, \eta^4\text{-SC}_4\text{H}_4)(\text{Y})_2$ ($\text{M} = \text{Ir}$, $\text{Y} = \text{BPh}_4$; $\text{M} = \text{Rh}$, $\text{Y} = \text{PF}_6$) are obtained by reaction of thiophene with either $[(\text{triphos})\text{Ir}(\eta^4\text{-C}_6\text{H}_6)]\text{BPh}_4$ in Me_2SO at 80°C or $[(\text{triphos})\text{RhCl}(\text{C}_2\text{H}_4)] + \text{TIPF}_6$ in THF at room temperature; a single-crystal X-ray diffraction analysis of the iridium complex shows that an open C₄H₄S moiety sits astride two metal centres; the bridge-bonding mode implies the sharing of four electron pairs with the metals.

Thiophene **T** is the simplest model substrate that organometallic chemists use in their effort to elucidate the main mechanistic pathways involved in the hydrodesulfurization (HDS) reaction of fossil fuels.¹

Several C–S bond scission reactions of **T** assisted by soluble metal complexes have been reported.¹ In some cases, the insertion products are bimetallic systems, which suggests a cooperative effect of more than one metal in the C–S bond cleavage on HDS catalysts.²

In a previous paper,³ we have shown that the η^4 -benzene complex $[(\text{triphos})\text{Ir}(\eta^4\text{-C}_6\text{H}_6)]\text{BPh}_4$ **1** in THF reacts with **T** to give the iridathiabenzene complex $[(\text{triphos})\text{Ir}(\eta^2\text{-C}_3\text{S-SC}_4\text{H}_4)]\text{BPh}_4$ **2** [$\text{triphos} = \text{MeC}(\text{CH}_2\text{PPh}_2)_3$] (Scheme 1). We report here that substitution of THF with Me_2SO dramatically changes the course of the reaction as the dimer $[(\text{triphos})\text{Ir}]_2(\mu\text{-}\eta^3, \eta^4\text{-SC}_4\text{H}_4)(\text{BPh}_4)_2$ **3** is selectively obtained as lemon-yellow crystals. An X-ray diffraction analysis for **3** shows that in the binuclear dication the C₄H₄S unit sits astride two metal centres in an unprecedented bonding network (Fig. 1).[†] Two pyramidal fragments of the ML_3 type (pseudo-symmetrically related to each other)[‡] appear concertedly inserted into a former C–S linkage of thiophene. The bonding capabilities of the open chain C₄H₄S are such as to allow the pseudo-octahedral coordination of both metals, hence to permit the 18-electron configuration of them both. In fact, the carbon and sulfur atoms, which were formerly connected in **T**, now lie in two distinct *trans*-axial positions with respect to the two triphos ligands. In the equatorial plane, Ir(2) is η^2 -coordinated by a C=S bond,⁴ whereas Ir(1) is η^3 -coordinated by the allylic moiety formed by the atoms C(2), C(3), C(4). With respect to a classical C₃H₅ allyl, one of the terminal H substituents is replaced by the C=S residue [the C(1)–C(2) separation is



Scheme 1

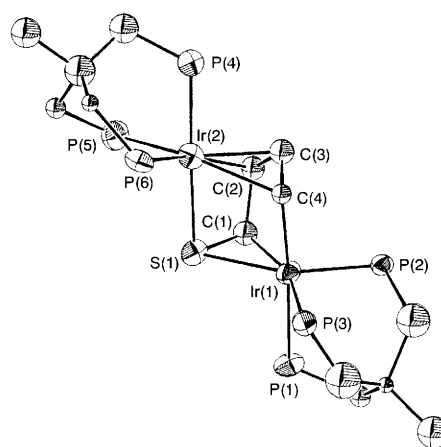
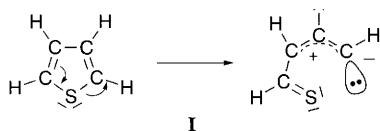


Fig. 1 ORTEP drawing of the complex cation in **3**. All of the hydrogen atoms and phenyl rings of triphos are omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): Ir(1)–S(1) 2.37(1), Ir(2)–S(1) 2.43(1), Ir(1)–C(1) 2.06(3), Ir(1)–C(4) 2.10(4), Ir(2)–C(2) 2.29(3), Ir(2)–C(3) 2.22(3), Ir(2)–C(4) 2.39(5), S(1)–C(1) 1.76(4), C(1)–C(2) 1.60(4), C(2)–C(3) 1.38(5), C(3)–C(4) 1.37(5); Ir(1)–C(1)–S(1) 76(1), Ir(1)–C(1)–C(2) 106(2), Ir(2)–S(1)–C(1) 89(1), Ir(2)–C(2)–C(1) 99(2), Ir(2)–C(2)–C(3) 69(2), S(1)–Ir(1)–C(1) 46(1), S(1)–Ir(1)–C(4) 78(1), S(1)–Ir(2)–C(2) 68.0(8), S(1)–Ir(2)–C(3) 86.4(9), S(1)–Ir(2)–C(4) 72(1), S(1)–C(1)–C(2) 104(2), C(1)–C(2)–C(3) 117(3), C(2)–C(3)–C(4) 114(3), C(1)–Ir(1)–C(4) 81(1), P(1)–Ir(1)–C(4) 175(2), P(2)–Ir(1)–S(1) 154.9(5), P(3)–Ir(1)–C(1) 159(1), P(5)–Ir(2)–C(4) 156(1), P(6)–Ir(2)–C(2) 167.8(9), P(4)–Ir(2)–S(1) 172.0(5).

consistent with a single bond], while on the opposite side one hydrogen is replaced by the whole Ir(1) fragment. If the cleavage of one C–S bond is heterolytic with charge redistribution as schematized in **I**, it is evident that C(4) becomes a two-electron σ -donor for Ir(1) while Ir(2) shares two electron pairs with the allylic moiety.



Significantly, the bonding to the metals of the open thiophene involves a total of 8 electrons, not 6. Indeed, if rather than a simple back-donation, an actual metal oxidation is implied ($d^8 \rightarrow d^6$, cationic \rightarrow anionic allyl), the open thiophene becomes a formal 8-electron donor.

The rhodium analogue of **3**, namely $\{[(\text{triphos})\text{Rh}]_2(\mu-\eta^3, \eta^4\text{-SC}_4\text{H}_4)\}(\text{PF}_6)_2$ **4**, is obtained as red crystals by treatment of $\{[(\text{triphos})\text{RhCl}(\text{C}_2\text{H}_4)]\}_5$ **5** in THF with TlPF₆ in the presence of an excess of **T**.

A comparison of the NMR characteristics of **3** and **4** readily shows that the two compounds share the same structure, and that **3** maintains in solution the structure determined in the solid state. § In particular, the lack of symmetry in both complexes is clearly shown by the magnetic inequivalence of the phosphorus atoms which give rise to ³¹P NMR ABDEGI (Ir) and ACEGIKXZ (Rh) splitting patterns. A slight second-order effect perturbs the spectrum of **3**, which has successfully been computed with the Davins program.⁶

The chemical shifts and coupling constants of the C₁H₁–C₂H₂–C₃H₃–C₄H₄ sequence have been determined unambiguously in both compounds by means of a variety of NMR experiments. Irrespective of the metal centre, the most deshielded carbon nucleus is the central allylic one, [$\delta(\text{C}_3)$ 119.9 in **3**, 118.2 in **4**], whereas the most shielded is the external allylic one [$\delta(\text{C}_2)$ 55.6 in **3**, 66.0 in **4**]. The other allylic carbon atom [$\delta(\text{C}_4)$ 58.2 in **3**, 102.9 in **4**], resonates at lower field as a consequence of its carbenoid character. As expected, the $J(\text{CP})$ coupling constants are larger for the carbon nuclei *transoid* to phosphorus atoms [$J(\text{C}_4\text{P})$ 88.9, $J(\text{C}_1\text{P})$ 55.5 Hz in **3**; $J(\text{C}_4\text{P})$ 98.0, $J(\text{C}_1\text{P})$ 55.4 Hz in **4**], consistent with the orientation of the C–M–P vectors determined in the solid-state structure.

A preliminary mechanistic study of the formation of **3** has been carried out. Unlike a precedent case of dimerization of a metallathiabenzene complex,^{2d} **3** does not form from the mononuclear complex **2** which, in fact, is stable in Me₂SO at 80 °C, even in the presence of an equivalent amount of the $\{[(\text{triphos})\text{Ir}]^+\}$ fragment (generated *in situ* by thermolysis of **1**) (Scheme 1). A crucial role in the formation of **3** is probably played by Me₂SO which is a better ligand than THF and may coordinate to the iridium metal, thus changing the electronic structure of the metal fragment initially interacting with **T**. The formation of **4** does not require the use of Me₂SO. In case of rhodium, the role of the coordinating solvent may be played by the ethylene ligand in the starting complex **5**.

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Footnotes

† Crystal data for **3**: C₁₃₄H₁₂₂B₂Ir₂P₆S, $M = 2356.39$, monoclinic, space group Cc , $a = 35.489(7)$, $b = 16.424(6)$, $c = 24.807(9)$ Å, $\beta = 117.35(4)^\circ$, $Z = 4$, $D_c = 1.22$ g cm⁻³, $R = 0.0782$ for 5668 independent reflections. Absorption correction was applied *via* ψ scan with absorption factors ranging from 2.333 to 1.001. The choice of the space group Cc was supported by the statistics on the intensities, which indicated unambiguously an acentric pattern. The phase problem was solved by direct methods (SIR92).⁷ Although the space group is acentric, a pseudo-symmetry problem affects the complex cation. A restrained least-squares refinement on F^2 was performed using SHELXL93.⁸ Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

‡ Their symmetry relationship ($x, y, z \rightarrow -x, y, 1/2 - z$) is actually of the space group C_2/c , whereas the bridging thiophene molecule is inconsistent with the presence of the inversion centre. This situation is responsible for the uncertain refinement of the crystal structure.

§ Selected NMR data (23 °C, CD₂Cl₂, J/Hz) for **3**: ³¹P{¹H} NMR (81.0 MHz) δ -0.2 (td, P_G), -24.0 (m, P_D), -25.3 (tt, P_E), -29.0 (m, P_A–P_B), -34.3 (m, P_I), $J(\text{P}_G\text{P}_D)$ 1.27, $J(\text{P}_G\text{P}_E)$ 17.44, $J(\text{P}_G\text{P}_A)$ -0.74, $J(\text{P}_G\text{P}_B)$ 10.21, $J(\text{P}_G\text{P}_I)$ 19.04, $J(\text{P}_D\text{P}_E)$ 18.27, $J(\text{P}_D\text{P}_A)$ 22.23, $J(\text{P}_D\text{P}_B)$ -0.88, $J(\text{P}_D\text{P}_I)$ 9.13, $J(\text{P}_E\text{P}_A)$ 4.42, $J(\text{P}_E\text{P}_B)$ 0.14, $J(\text{P}_E\text{P}_I)$ 4.60, $J(\text{P}_A\text{P}_B)$ 4.88, $J(\text{P}_A\text{P}_I)$ -1.28, $J(\text{P}_B\text{P}_I)$ 24.46; ¹H NMR (200.1 MHz) δ 5.51 (m, H₁), 5.03 (m, H₂), 4.40 (m, H₄), 3.30 (m, H₃), $J(\text{H}_1\text{H}_2)$ 4.3, $J(\text{H}_2\text{H}_3)$ 3.1, $J(\text{H}_2\text{H}_4)$ 2.1, $J(\text{H}_3\text{H}_4)$ 5.9; ¹³C{¹H} NMR (50.3 MHz) δ 119.9 (br s, C₃), 65.9 [d, $J(\text{CP})$ 55.5, C₁], 58.2 [dd, $J(\text{CP})$ 88.9, 18.8, C₄], 55.6 [dd, $J(\text{CP})$ 22.9, 6.6, C₂].

For **4**: ³¹P{¹H} NMR (81.0 MHz) δ 28.7 (dddd, P_A), 14.6 (dddd, P_C), 5.3 (dddt, P_E), -1.6 (ddd, P_G), -2.6 (ddt, P_I), -7.8 (dtdd, P_K), $J(\text{P}_A\text{P}_C)$ 3.65, $J(\text{P}_A\text{P}_E)$ 20.16, $J(\text{P}_A\text{P}_K)$ 33.71, $J(\text{P}_A\text{Rh})$ 139.5, $J(\text{P}_C\text{P}_E)$ 27.03, $J(\text{P}_C\text{P}_I)$ 34.73, $J(\text{P}_C\text{P}_K)$ 12.46, $J(\text{P}_C\text{Rh})$ 89.7, $J(\text{P}_E\text{P}_I)$ 7.49, $J(\text{P}_E\text{P}_K)$ 6.98, $J(\text{P}_E\text{Rh})$ 124.7, $J(\text{P}_G\text{P}_I)$ 8.53, $J(\text{P}_G\text{P}_K)$ 36.79, $J(\text{P}_G\text{Rh})$ 104.0, $J(\text{P}_I\text{Rh})$ 119.2, $J(\text{P}_K\text{Rh})$ 76.1; ¹H NMR (200.1 MHz) δ 5.35 (m, H₁), 4.93 (m, H₂), 4.84 (m, H₄), 4.21 (m, H₃), $J(\text{H}_1\text{H}_2)$ 4.1, $J(\text{H}_1\text{Rh})$ 1.2, $J(\text{H}_2\text{H}_3)$ 3.1, $J(\text{H}_2\text{Rh})$ 2.0, $J(\text{H}_3\text{H}_4)$ 5.3, $J(\text{H}_3\text{Rh})$ 2.0, $J(\text{H}_4\text{Rh})$ 2.4; ¹³C{¹H} NMR (50.3 MHz) δ 118.2 (br s, C₃), 102.9 [dt, $J(\text{CP})$ 98.0, 25.0, C₄], 77.7 [dd, $J(\text{CP})$ 55.4, 15.6, C₁], 66.0 [br d, $J(\text{CP})$ 27.6, C₂].

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