

Preliminary communication

Formation of 2-thienyl derivatives during the thermal activation
of thiophene by $\text{Tp}^* \text{Ir}(\text{C}_2\text{H}_4)_2$ Margarita Paneque ^a, Manuel L. Poveda ^a, Luis Rey ^a, Soraya Taboada ^a, Ernesto Carmona ^{a,*},
Caridad Ruiz ^{b,c}^a Departamento de Química Inorgánica–Instituto de Ciencia de Materiales,

Universidad de Sevilla–Consejo Superior de Investigaciones Científicas, Apdo 553, 41071 Sevilla, Spain

^b Instituto de Ciencia de Materiales, Sede D, Consejo Superior de Investigaciones Científicas, Serrano 113, 28006 Madrid, Spain^c Facultad de Ciencias Químicas, Universidad Complutense, 28040 Madrid, Spain

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Abstract

The reaction of thiophene with $[\text{Tp}^* \text{Ir}(\text{C}_2\text{H}_4)_2]$ (Tp^* = hydrotris(3,5-dimethylpyrazolyl)borate ligand) at 60°C results in the incorporation of three molecules of the heterocycle, two in the form of 2-thienyl fragments and the third S-coordinated to the Ir atom in its intact form, e.g. $[\text{Tp}^* \text{Ir}(\text{2-thienyl})_2(\text{SC}_4\text{H}_4)]$ **2**. The reactions of **2** with PMe_3 , CO and H_2 have been investigated. The molecular structure of the binuclear hydride $\{[\text{Tp}^* \text{Ir}(\text{H})]_2(\mu\text{-H})(\mu\text{-S}, \text{C-SC}_4\text{H}_3)\}$ **6** has been determined by X-ray studies.

Keywords: Thiophene activation; Thienyl bridges

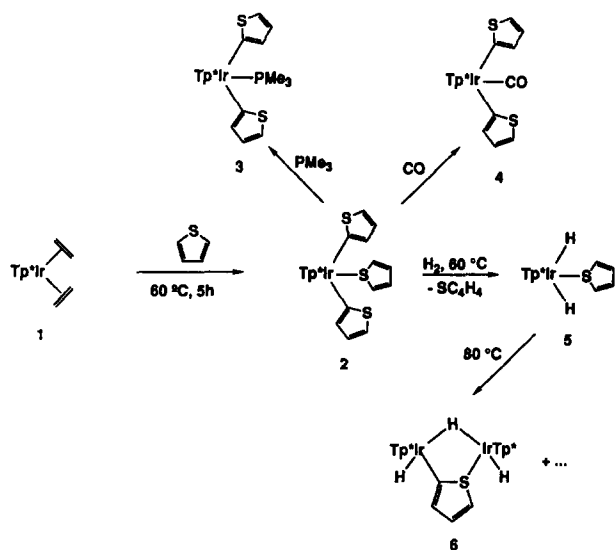
The chemistry of thiophene derivatives of the transition metals has progressed very rapidly in the last few years mainly because of the potential utility of these compounds as molecular models for the complex heterogeneous reaction involved in the hydrodesulfuration process [1]. Different thiophene coordination modes and reactivity patterns have been observed [1–3]. Our interest in the activation of the C–H bonds of organic substrates [4] by Rh and Ir complexes of the potentially tridentate hydrotris(3,5-dimethylpyrazolyl)borate ligand, Tp^* , has led us into the field of thiophene activation. Here we report that the thermal reaction of $[\text{Tp}^* \text{Ir}(\text{C}_2\text{H}_4)_2]$ **1** with thiophene proceeds with formation of the complex $[\text{Tp}^* \text{Ir}(\text{C}=\text{CH}-\text{CH}=\text{CH}-\text{S})(\eta^1\text{-SC}_4\text{H}_4)]$ **2**, which incorporates three molecules of thiophene, one intact, S-coordinated to the Ir center, the other two metallated in the form of 2-thienyl fragments. The chemical reactivity of compound **2** (Scheme 1) is also discussed.

Whereas treatment of a THF solution of **1** with an excess of thiophene (≥ 10 equiv.), at 60°C, leads to a complex mixture of products, the reaction of **1** with neat

thiophene at the same temperature takes place almost quantitatively to afford amber crystals of **2** as the only isolable product. In accord with previous studies [4], the analogous transformation of the hydrido-vinyl $[\text{Tp}^* \text{IrH}(\text{CH}=\text{CH}_2)(\text{C}_2\text{H}_4)]$, photochemically generated from **1**, with pure thiophene proceeds similarly and also yields compound **2**. In the solid state **2** seems to be indefinitely stable with respect to loss of the coordinated thiophene and it is moderately air stable too. Thiophene solutions of **2** are also indefinitely stable when kept under N_2 . In other common organic solvents, however, the coordinated thiophene is slowly dissociated. Analytical data [5] and the chemical reactivity of **2**, summarized in Scheme 1 and discussed below, are in accord with the proposed formulation. However, owing to restricted rotation of the thienyl ligands of this complex and to its limited thermal stability in solution, the variable temperature ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR data [6] prove of little help in establishing unambiguously the structure of this complex.

The lability of the thiophene ligand in **2** allows its replacement by other neutral molecules. Petroleum ether solutions of **2**, stirred under N_2 , display a strong IR absorption in the vicinity of 2215 cm^{-1} , which, by comparison with the related species $[\text{Tp}^* \text{Ir}(\text{C}_6\text{H}_5)_2(\text{N}_2)]$

* Corresponding author.



Scheme 1.

[4c], can be tentatively assigned to $\nu(\text{N}\equiv\text{N})$ of a weakly bound N_2 molecule in the adduct $[\text{Tp}^*\text{Ir}(\text{2-thienyl})_2(\text{N}_2)]$. In accord with the high N–N stretching frequency, this compound exhibits poor thermal stability and cannot be isolated in a pure form. In the presence of a 2-fold excess of PMe_3 , complex **2** converts into the corresponding adduct, $[\text{Tp}^*\text{Ir}(\text{2-thienyl})_2(\text{PMe}_3)]$ **3**. 1D and 2D NMR studies [6] confirm the presence of the 2-thienyl ligands and reveal in addition the existence in solution of equilibrium mixtures of three different rotamers arising from restricted rotation of the $\sigma\text{-C}_4\text{H}_3\text{S}$ fragments around the Ir–C bond. For two of these, the 2-thienyl fragments are equivalent by symmetry, while the third exhibits non-equivalent thienyls. In accord with this, three closely spaced singlets at $\delta -55.0$, -55.1 and -55.5 ppm (intensity ratio 1:4:2) can be observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. When solutions of **2** are stirred under 2 atm of CO, the expected carbonyl adduct $[\text{Tp}^*\text{Ir}(\text{2-thienyl})_2(\text{CO})]$ **4** is obtained. Once again, spectroscopic data [6] reveal the existence of different isomers, indicated for instance in the observation of two $\nu(\text{C}=\text{O})$ bands in the IR spectrum in the range $2050\text{--}2030\text{ cm}^{-1}$. The structure of **4** has been determined by X-ray crystallography and will be reported later.

Hydrogenation of **2** at 60°C (2 atm of H_2) furnishes the dihydride $[\text{Tp}^*\text{Ir}(\text{H})_2(\text{SC}_4\text{H}_4)]$ **5** [6] along with free thiophene. Small amounts of the known [7] $[\text{Tp}^*\text{IrH}_4]$ are also formed, the latter species becoming the only reaction product when the hydrogenation of **2** is effected at 90°C . Upon heating concentrated solutions of **5** in the absence of H_2 , a new reaction occurs to yield the binuclear species $\{[\text{Tp}^*\text{IrH}]_2(\mu\text{-H})(\mu\text{-S,C-SC}_4\text{H}_3)\}$ **6** as the main reaction product (ca. 50% yield; see Scheme 1). Smaller quantities of $[\text{Tp}^*\text{Ir}(\text{H})_4]$ and of

another hydride derivative, whose nature is currently under investigation, are also produced.

The binuclear compound **6** can be readily separated from the reaction mixture by fractional crystallization and its structure can be ascertained by NMR spectroscopy. The observation of 12 Me singlets for the coordinated Tp^* ligands and of three high-field hydride resonances at $\delta -23.23$ (d), -24.29 (d) and -30.76 (t), with relative intensities 1:1:1, are in agreement with the existence of two, non-symmetry related Tp^*Ir moieties. The 2-thienyl fragment gives rise to a single set of sharp resonances (two doublets and a doublet of doublets between 6.5 and 7.1 ppm), suggesting that the ring is no longer free to rotate around the Ir–C bond. These data are in accord with the structure shown in Scheme 1, which has been unequivocally established by an X-ray study [8]. An ORTEP representation of the molecules of **6** is shown in Fig. 1, which also includes the atom labelling scheme. As can be seen, the two $\text{Tp}^*\text{Ir}(\text{H})$ moieties are bridged by a hydride and by a 2-thienyl fragment, the latter acting as an η^2 -ligand, C- and S-bound, respectively, to the two Ir atoms. To our knowledge this is an unprecedented coordination for a 2-thienyl ligand. Owing to the positional disorder that involves the activated thiophene ring, the refinement of the structure has been carried out in the $C2/c$ group, with constrained populations factors of 0.5 for the C(4) and the S(1) atoms both in the same position. For this reason, comparison of the bond lengths of this fragment with those of other structurally characterized 2-thienyls does not seem appropriate. The bridging hydride atom was located in a final Fourier difference synthesis at a distance of $1.91(17)\text{ \AA}$ from each Ir center. The complex is best described as an Ir(III)–Ir(III) system, and it is characterized by an Ir–Ir distance of $3.066(1)\text{ \AA}$. This compares well with the corresponding distances found in other $\text{Ir}(\mu\text{-H})\text{Ir}$ systems [9]. For example, in the complex $\{[\text{Cp}^*\text{IrCl}]_2(\mu\text{-H})(\mu\text{-Cl})\}$ [10], which also has

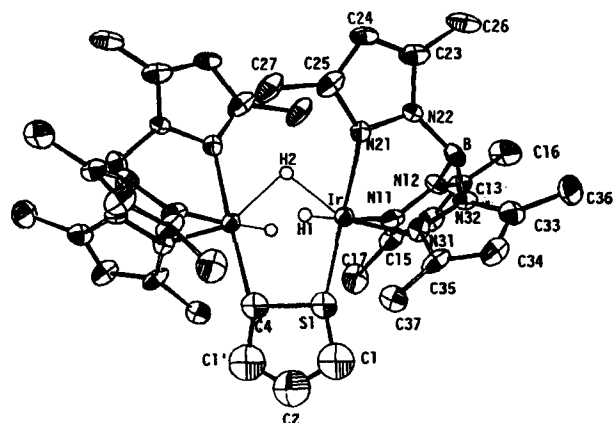


Fig. 1. ORTEP drawing of compound **6** and atom labelling scheme, showing the thermal ellipsoids at 20% probability.

a single hydride bridge, the Ir–Ir separation amounts to 2.903(1) Å. As in the latter compound, the IrHIr moiety of **6** forms a two-electron three-center bond that involves significant Ir–Ir bonding interaction [11].

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 - [5] Satisfactory analytical data have been obtained for all new compounds.
 - [6] NMR data for **2**: ^1H NMR (CD_2Cl_2 , -40°C) complex resonances between δ 7.6 and 6.7, and at δ 5.6 for the thienyl and thiophene protons.
Selected NMR data for **3** (main rotamer): ^1H NMR (CD_2Cl_2 , 20°C) δ 7.16 (1 H, dd, $^3J(\text{H-H}) = 4.9$; $^4J(\text{H-H}) = 0.7$ Hz), 6.71 (1 H, dd, $^3J(\text{H-H}) = 4.9$, 3.1 Hz) and 5.85 (1 H, dd, $^3J(\text{H-H}) = 3.1$; $^4J(\text{H-H}) = 0.7$ Hz), (3 CH of a thienyl moiety); 7.14 (1 H, dd, $^3J(\text{H-H}) = 4.2$; $^4J(\text{H-H}) = 0.9$ Hz), 6.90 (1 H, dd, $^3J(\text{H-H}) = 4.2$, 3.2 Hz) and 7.37 (1 H, dd, $^3J(\text{H-H}) = 3.2$; $^4J(\text{H-H}) = 0.9$ Hz), (3 CH of a second thienyl ligand). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 20°C) δ -55.1 . $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 20°C) δ 120.2 (d, $^2J(\text{CP}) = 10$ Hz, Ir–C), 123.1, 125.9 and 134.6 (a thienyl ring); 123.7 (d, $^2J(\text{CP}) = 10$ Hz, Ir–C), 124.9, 125.8 and 135.0 (a second thienyl ligand).
Selected NMR data for **4** (main rotamer): ^1H NMR (CD_2Cl_2 , -40°C) δ 7.25 (1 H, dd, $^3J(\text{H-H}) = 5.0$; $^4J(\text{H-H}) = 1.0$ Hz), 6.76 (1 H, dd, $^3J(\text{H-H}) = 5.0$, 3.3 Hz) and 5.80 (1 H, dd, $^3J(\text{H-H}) = 3.3$; $^4J(\text{H-H}) = 1.0$ Hz), (3 CH of a thienyl moiety); 7.50 (1 H, dd, $^3J(\text{H-H}) = 3.3$; $^4J(\text{H-H}) = 0.9$ Hz), 7.19 (1 H, dd, $^3J(\text{H-H}) = 5.0$; $^4J(\text{H-H}) = 0.9$ Hz) and 6.95 (1 H, dd, $^3J(\text{H-H}) = 5.0$, 3.3 Hz) (3 CH of a second thienyl ligand). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 – C_6D_6 , 60°C) δ 166.1 (CO), 119.4 (Ir–C), 126.5, 126.8 and 133.1 (thienyl rings).
Selected NMR data for **5**: ^1H NMR (C_6D_6 , 20°C) δ -20.41 (2 H, s, Ir–H); 6.55 (2 H, m) and 7.08 (2 H, m) (AA'XX' system, thiophene ligand). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 20°C) δ 128.2 (2 CH of thiophene), 136.9 (2 CH of thiophene).
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 - [8] Crystallographic data for **6**: $a = 19.955(6)$, $b = 13.310(3)$, $c = 15.677(3)$ Å; $\beta = 107.42(2)^\circ$ with $Z = 4$. Data collected at -100°C . Crystals of **6** are monoclinic, space group $C2/c$. $R(F) = 0.052$ and $R_w(F) = 0.060$ with 2623 reflections [$I < 2\sigma(I)$]. Final refinement with unit weights and anisotropic thermal motion for all atoms except S(1), C(4), C(1), C(2) and hydrogen atoms that have been refined isotropically. The hydrogen atoms were included with fixed isotropic contributions at their calculated positions, except the H(2) hydride atom, which was located in a final Fourier difference synthesis and their coordinates were subsequently refined. Most of the calculations were carried out with the X-Ray 80 system: J.M. Stewart, *The X-Ray 80 System*, Computer Science Center, University of Maryland, College Park, MD, 1985.
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