Preliminary communication

ORGANOMETALLIC MODELS FOR THE HYDRODESULPHURISATION (HDS) REACTION: SYNTHESIS OF [(η-thiophene)M(PPh$_3$)$_2$]$^+$ (M = Rh, Ir) AND X-RAY STRUCTURE OF THE Rh DERIVATIVE, THE FIRST EXAMPLE OF A FULLY CHARACTERISED π-THIOPHENE COMPLEX OF AN HDS-ACTIVE METAL

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Summary

Hydrogenation of [(NBD)M(PPh$_3$)$_2$][PF$_6$] (M = Rh, Ir; NBD = norbornadiene) in CH$_2$Cl$_2$/thiophene gives [(η-thiophene M(PPh$_3$)$_2$]$^+$ (M = Rh, Ir) compounds, which have been isolated and characterised. In the case of [(η-thiophene)-Rh(PPh$_3$)$_2$]$^+$ the structure has been determined by X-ray diffraction; the cation involves a trigonal arrangement of two phosphines and a π-bonded thiophene around the Rh atom. Crystal data: triclinic, space group P$\bar{1}$, *a* 11.774(6), *b* 18.083(8), *c* 11.425(5) Å, α 75.24(2), β 105.48(2), γ 103.24(2)°, *U* 2227(2) Å^3, and Z = 2. The coordinated thiophene is readily displaced by donor ligands from the Rh complex, but is strongly bound in the Ir analog.

Hydrodesulphurisation (HDS) of fossil fuel feedstocks can arguably be considered the most important chemical reaction practised in industry [1]. Heavy petroleum fractions and coal-derived liquids contain sulphur predominantly in the form of thiophene derivatives, and so HDS of thiophene, benzothiophene, and dibenzothiophene over heterogeneous catalysts has been extensively investigated [1]. Nevertheless, many fundamental mechanistic questions, such as the mode of bonding of thiophene to the surface and the elementary steps following adsorption, remain

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essentially unanswered. Both S-atom coordination and π-bonding to the surface have been suggested on the basis of experimental and theoretical arguments, but owing to the complexity of the heterogeneous system it has not been possible to reach a definite conclusion [1]. Recent theoretical studies favored S-only coordination, and the absence of π-thiophene complexes of HDS-active metals in the literature was taken as further support for this view [2].

Recently Spies and Angelici have proposed a π-bonded structure for [(η-C_4H_4S)-Ru(η-C_5H_5)]BF_4 on the basis of chemical and spectroscopic data [3]. In this communication we report the first example of a fully characterised π-thiophene complex of an HDS-active (4d or 5d) metal, viz. [(η-C_4H_4S)Rh(PPh$_3$)$_2$]$^+$. The complex was prepared by bubbling hydrogen through a solution of [(NBD)Rh-(PPh$_3$)$_2$][PF$_6$] [4] (0.5 g, 0.58 mmol) in CH_2Cl_2 (5 cm^3)/thiophene (5 cm^3, 63.3 mmol). After 40 min the colour of the solution had changed from orange to red; addition to diethyl ether and cooling to $-20°C$ overnight gave red crystals of [(η-C_4H_4S)Rh(PPh$_3$)$_2$][PF$_6$] · 2(C_4H_4S) (1) suitable for an X-ray diffraction study (70% yield). 1 gave correct C, H, P analysis: ^{1}H NMR (CDCl$_3$) δ, Me$_4$Si, 7.33 (m, thiophene H(2,5)), 7.53 (m, thiophene H(3,4)), 7.43 ppm (m, (PPh$_3$)); ^{31}P {^{1}H} NMR (CDCl$_3$) δ, H$_3$PO$_4$, 40.2 (d, J(Rh–P) 205 Hz); IR: ν(PF) 845 (br) cm^{-1}; m.p. 156–160°C (dec).

The Ir analog [(η-thiophene)Ir(PPh$_3$)$_2$][PF$_6$] (2) was similarly synthesized (90% yield), and isolated as large yellow prisms which became opaque and fragmented upon isolation from the solution. Identification of 2 was therefore based on correct C, H, P, S analyses and ^{1}H NMR spectra (CDCl$_3$) δ, Me$_4$Si, 7.11 (m, thiophene H(2,5)), 7.43 (m, thiophene H(3,4)), 7.33 ppm (m, PPh$_3$), by analogy with 1.

Crystal data for 1: $C_{40}H_{34}F_6P_3RhS$ · $2C_4H_4S$, $M = 1024.86$, triclinic, space group $P\bar{1}$, a 11.744(6), b 18.083(8), c 11.425(5) Å, α 75.24(2), β 105.48(2), γ 103.24(2)°, U 2227(2) Å^3, $Z = 2$, D_c 1.528 g cm^{-3}, $F(000) = 1044$, λ 0.71069 Å, μ(Mo-K_α) 6.76 cm^{-1}. The intensities of 7520 independent reflections were measured on a Siemens AED diffractometer, with θ in the range 3–24°, using the $\theta/2\theta$ scan technique and niobium-filtered Mo-K_α radiation. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares on the basis of 4441 observed reflections [$I \geq 2\sigma(I)$] with anisotropic thermal parameters for all the non-hydrogen atoms except those of the thiophene molecules of crystallization, which were found to show some disorder. The hydrogen atoms (placed at their geometrically calculated positions) of the cation were introduced, but not refined, in the final structure factor calculations. Final R and R_w values 0.062 and 0.084 *.

The structure of 1 consists of [(η-C_4H_4S)Rh(PPh$_3$)$_2$]$^+$ cations (Fig. 1), PF$_6^-$ anions, and thiophene molecules of crystallization. The main feature of this structure is the π-bonding of the thiophene ligand to the rhodium atom in the cation. The Rh is in a trigonal arrangement if the centroid of the thiophene (C_t) is regarded as a coordination site, with the other two sites occupied by the two P atoms from the PPh$_3$ ligands. The Rh atom is at a distance of 1.917 Å from C_t, and the values of the P(1)–Rh–C_t and P(2)–Rh–C_t angles are 129.2 and 133.1°, respectively. The
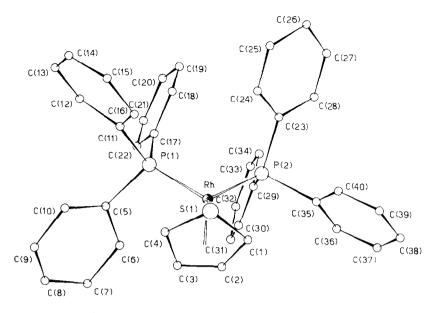

Fig. 1. View of the cation in $[(\eta\text{-}C_4H_4S)Rh(PPh_3)_2][PF_6]\cdot 2(C_4H_4S)$. Selected bond distances (Å) and angles (°): Rh–P(1) 2.254(3), Rh–P(2) 2.239(2), Rh–S(1) 2.567(3), Rh–C(1) 2.238(12), Rh–C(2) 2.239(15), Rh–C(3) 2.259(12), Rh–C(4) 2.249(9), S(1)–C(1) 1.734(15), S(1)–C(4) 1.731(10), C(1)–C(2) 1.40(2), C(2)–C(3) 1.38(2), C(3)–C(4) 1.43(2); P(1)–Rh–P(2) 96.9(1), C(1)–S(1)–C(4) 90.0(6), S(1)–C(1)–C(2) 112(1), C(1)–C(2)–C(3) 113(1), C(2)–C(3)–C(4) 112(1), C(3)–C(4)–S(1) 112(1).

thiophene ligand is only roughly planar, the deviations of S(1), C(1), C(2), C(3), C(4) from the mean plane passing through them being −0.014(4), 0.103(12), −0.046(13), −0.068(12), 0.092(10) Å, respectively.

The only other reported structure of a thiophene complex is that of $Cr(CO)_3(\eta\text{-}C_4H_4S)$ [5], which is less relevant to HDS in view of the low catalytic activity displayed by $3d$ metals in this reaction [1,2,6].

The coordinated thiophene in **1** is very labile in CH_2Cl_2 solution; addition of norbornadiene at 25°C immediately regenerates $[Rh(NBD)(PPh_3)_2]^+$ quantitatively, and bubbling of CO produces $[\textit{trans}\text{-}Rh(CO)_2(PPh_3)_2]^+$. The thiophene is more strongly bound in **2**, which does not react with NBD or COD at room temperature, and reacts only slowly with CO to yield $[Ir(CO)_2(PPh_3)_2]^+$. Such higher stability of Ir complexes with respect to their Rh analogs is normal. Strong coordination of thiophene was also observed in the case of $[(\eta\text{-thiophene})Ru(\eta\text{-}C_5H_5)]^+$ [3].

Chianelli and coworkers have shown that $3d$ metal sulphides show poor activity for HDS, whilst $4d$ and $5d$ metal sulphides are highly active, the maximum activity been found for Ru, Rh and Os, Ir, respectively [2a,6].

Our complexes **1** and **2** thus represent good models for thiophene chemisorption in that Rh and Ir are two of the most active HDS metals [2a,6,7]; furthermore, the structure of **1** shows that π-coordination of the thiophene molecule may, in fact, be dominant, in contrast to theoretical arguments which favour S-binding to metal sulphide surfaces [2]. The S-only type of coordination of thiophene to second or third row metals has only been proposed for the partially characterised

$[Ru(NH_3)_5(C_4H_4S)]^{2+}$ [8]. Two complexes containing S-bonded thiophenic fragments have been characterised crystallographically, namely the complexes $RuCl_2$(4-Ph_2P-DBT) [9], and $[(ThCH_2C_5H_4)Ru(PPh_3)_2]BF_4$ [10], which are less directly related to HDS substrates. We thus suggest that π-coordination of thiophene to metals in complexes and on surfaces may be more important than hitherto realised. We are currently extending this work to other metals and ligands relevant to HDS.

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