Organometallics **1997,** *16,* 2465−2471 2465

Homogeneous Hydrogenation of Benzo[*b*]thiophene by Use of Rhodium and Iridium Complexes as the Catalyst Precursors: Kinetic and Mechanistic Aspects[†]

Verónica Herrera,[‡] Alberto Fuentes,[‡] Merlín Rosales,[‡,§]
Roberto A. Sánchez-Delgado,*,[‡] Claudio Bianchini,[∥] Andrea Meli,[∥] and
Francesco Vizza[∥]

Instituto Venezolano de Investigaciones Científicas (IVIC), Centro de Química, Apdo. 21827, Caracas 1020-A, Venezuela, and Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione, CNR, Via J. Nardi 39, I-50132 Firenze, Italy

Received December 2, 1996[⊗]

The complexes $[M(COD)(PPh_3)_2]PF_6$ (M = Rh, **1a**; Ir, **1b**) are highly efficient precatalysts for the homogeneous hydrogenation of benzo[*b*]thiophene (BT) to 2,3-dihydrobenzo[*b*]thiophene (DHBT). Both complexes react rapidly with BT and H_2 to produce the corresponding $[M(H)_2(\eta^1(S)\text{-}BT)_2(PPh_3)_2]PF_6$ (M = Rh, **2a**; Ir, **2b**), which enter the catalytic cycle. In the case of Ir, the catalysis is more conveniently carried out by use of **2b**, which is stable enough to be isolated pure. Kinetic and mechanistic studies of BT hydrogenation were carried out by using **1a** and **2b** as the catalyst precursors in 1,2-dichloroethane solution at 40 °C. For both complexes, the reaction proceeds according to the rate law $r = k_{cat}\,[M]\,[H_2]$, where $k_{cat} = k_1K_3/(1 + K_3[H_2])$. All of the experimental data are consistent with a general mechanism in which the transfer of the hydrides to coordinated BT in $[M(H)_2(\eta^2(C{=}C)\text{-}BT)(PPh_3)_2]PF_6$ is the rate-determining step of the catalytic cycle. The complex $[Ir(H)_2(\eta^1(S)\text{-}DHBT)_2(PPh_3)_2]PF_6$ was obtained as a stable end product of the Ir catalysis and was characterized by spectroscopic analysis and by X-ray diffraction. The coordination geometry around the iridium atom consists of a distorted octahedron with mutually *cis* S-bonded DHBT, *cis* hydrides, and *trans* triphenylphosphines.

Introduction

The homogeneous hydrogenation of sulfur-containing aromatic compounds by transition metal complexes is of interest in relation to the mechanisms involved in the industrially important hydrodesulfurization (HDS) process.[1] A number of Ru, Os, Rh, and Ir complexes catalyze the regioselective hydrogenation of benzo[*b*]thiophene (BT) to 2,3-dihydrobenzo[*b*]thiophene (DHBT).[2,3] Only one report deals with the hydrogenation of thiophene to tetrahydrothiophene,[4] while no example of the hydrogenation of dibenzo[*b,d*]thiophene (DBT) has been reported so far.

For BT hydrogenation, two mechanisms have been discussed in the literature. Fish and co-workers,[2f] based on detailed NMR studies and deuteration experiments, have elucidated a catalytic cycle for $[Rh(\eta^5\text{-}Cp^*)(MeCN)_3]^{2+}$ involving η^2-coordination of BT to a Rh(III) polyhydride, followed by hydride transfers to the $C_2{=}C_3$ bond of BT to give an η^6-bonded DHBT, which is displaced by a new BT molecule to restart the cycle. Sanchez-Delgado et al.[3c] determined the mechanism for $[Rh(COD)(PPh_3)_2]PF_6$ (**1a**) (COD = 1,5-cyclooctadiene) employing a combination of kinetic, chemical, and theoretical methods. The catalyst precursor reacts with H_2 and BT to yield $[Rh(H)_2(\eta^1(S)\text{-}BT)_2(PPh_3)_2]PF_6$ (**2a**), which then dissociates a BT ligand to enter the cycle. This proposal also invokes η^2-coordination of the substrate, followed by the rate-determining hydride transfer to the $C_2{=}C_3$ bond of BT to form $[Rh(\eta^1(S)\text{-}DHBT)(PPh_3)_2]^+$; at this point in the cycle, two pathways are available: (i) displacement of DHBT by BT to generate $[Rh(\eta^5\text{-}BT)(PPh_3)_2]^+$, which subsequently adds H_2, or (ii) addition of H_2 yielding $[Rh(H)_2(DHBT)(PPh_3)_2]^+$, followed by displacement of DHBT by BT; both reaction schemes regenerate the active η^2-BT intermediate. Although both mechanisms display similarities, an important difference is that Fish's proposal invokes dicationic Cp*Rh(III) intermediates containing one or more H ligands plus BT bonded to the metal; this

---

[†] In memory of Prof. G. Wilkinson.

[‡] IVIC.

[§] Permanent address: Inorganic Chemistry Laboratory, Chemistry Department, Facultad de Ciencias, Universidad del Zulia, Apdo. 526, Maracaibo, Venezuela.

[∥] CNR.

[⊗] Abstract published in *Advance ACS Abstracts,* April 15, 1997.

(1) (a) Schuman, S. C.; Shalit, H. *Catal. Rev.* **1970**, *4*, 245. (b) Mitchell, P. C. H. In *Catalysis*; Kemball, C., Ed.; The Chemical Society: London, 1977; Vol. 1, p 223. Mitchell, P. C. H. In *Catalysis*; Kembell, C., Ed.; The Chemical Society: London, 1981; Vol. 4, p 203. (c) Gates, B. C.; Katzer, J. R.; Schuit, G. C. A. *Chemistry of Catalytic Processes*; McGraw-Hill: New York, 1979. (d) Grange, P. *Catal. Rev.*−*Sci. Eng.* **1980**, *21*, 135. (e) Wiegand, B. C.; Friend, C. M. *Chem. Rev.* **1992**, *92*, 491. (f) López, R.; Peter, D.; Zdrazil, M. *Collect. Czech. Chem. Commun.* **1981**, *46*, 2185. (g) Girgis, M. J.; Gates, B. C. *Ind. Eng. Chem. Res.* **1991**, *30*, 2021. (h) Angelici, R. J. *Acc. Chem. Res.* **1988**, *21*, 387. (i) Angelici, R. J. *Coord. Chem. Rev.* **1990**, *105*, 61. (j) Angelici, R. J. *Bull. Soc. Chim. Belg.* **1995**, *104*, 265. (k) Sánchez-Delgado, R. A. *J. Mol. Catal.* **1994**, *86*, 287. Bianchini, C.; Meli, A. *J. Chem. Soc., Dalton Trans.* **1996**, 801.

(2) (a) Fish, R. H.; Thormodsen, A. D.; Cremer, G. A. *J. Am. Chem. Soc.* **1982**, *104*, 5234. (b) Fish, R. H. *Ann. N. Y. Acad. Sci.* **1983**, *415*, 292. (c) Fish, R. H.; Tan, J. L.; Thormodsen, A. D. *J. Org. Chem.* **1984**, *49*, 4500. (d) Fish, R. H.; Tan, J. L.; Thormodsen, A. D. *Organometallics* **1985**, *10*, 1743. (e) Fish, R. H.; Baralt, E.; Smith, S. J. *Organometallics* **1991**, *10*, 54. (f) Baralt, E.; Smith, S. J.; Hurwitz, J.; Horváth, I.; Fish, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 5187.

(3) (a) Sánchez-Delgado, R. A.; González, E. *Polyhedron* **1989**, *8*, 1431. (b) Sánchez-Delgado, R. A. In *Advances in Catalyst Design*; Graziani, M., Rao, C. N. R., Eds.; World Scientific Publishing Co.: Singapore, 1991; p 214. (c) Sánchez-Delgado, R. A.; Herrera, V.; Rincón, L.; Andriollo, A. Martín, G. *Organometallics* **1994**, *13*, 553.

(4) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Herrera, V.; Sánchez-Delgado, R. A. *Organometallics* **1994**, *13*, 721.

S0276-7333(96)01007-2 CCC: $14.00

suggests that Rh has to go through oxidation states higher than 3 at some point in the cycle, which is unusual. In Sanchez-Delgado's proposal, the Rh metal goes through the catalysis with the usual III−I−III reduction−oxidation changes; however, some features of this latter reaction mechanism could not be unambiguously established because of the low catalytic activities observed and the inherent instability of the intermediates participating in the cycle.

As early as 1989, some of us reported that the analogous iridium system, $[Ir(COD)(PPh_3)_2]PF_6$ (**1b**), was able to catalyze (albeit slowly) the hydrogenation of BT in THF solution under rather severe reaction conditions.[3a] Also, we have more recently shown that **1b** reacts rapidly with BT under 1 atm of H_2 in chlorinated solvents at room temperature to yield $[Ir(H)_2(\eta^1(S)\text{-BT})_2(PPh_3)_2]PF_6$ (**2b**),[5] which is a stable analogue of **2a**, one of the key intermediates proposed to intervene in the Rh-catalyzed hydrogenation of BT. In the present paper, we disclose further work on the kinetics and mechanism of the regioselective hydrogenation of BT catalyzed by complexes **1a** and **2b**, which are highly active in 1,2-dichloroethane solution under very mild reaction conditions. Also, we report the synthesis and X-ray structure of $[Ir(H)_2(\eta^1(S)\text{-DHBT})_2(PPh_3)_2]PF_6$ (**3b**), another key species related to the catalysis. These studies complement our previous reports on Rh catalysis and shed further light on the general mechanisms involved in this important transformation.

Experimental Section

Instruments and Materials. Solvents of analytical grade were distilled from the appropriate drying agents under N_2 immediately prior to use; iridium(III) trichloride hydrate (Alfa), ammonium hexafluorophosphate (Aldrich), and triphenylphosphine (Aldrich) were used without further purification; benzothiophene (Aldrich) was purified by recrystallization from ethanol/water. The complexes $[M(COD)(PPh_3)_2]PF_6$, M = Rh (**1a**) and Ir (**1b**),[6] and $[Ir(H)_2(BT)_2(PPh_3)_2]PF_6$ (**2b**)[5] were prepared according to published procedures. NMR spectra were obtained by using a Bruker AM-300 instrument. Hydrogen was purified by passing through two columns in series containing CuO/Al_2O_3 and $CaSO_4$, respectively. The apparatus for the catalytic runs has been previously described in detail.[3c,7]

Procedure for Kinetic Measurements. In a typical experiment, a solution of the catalyst and the substrate in 1,2-dichloroethane was placed in a jacketed glass reactor fitted with a reflux condenser kept at 0 °C. The reactor was sealed with Apiezon wax to a high-vacuum line, and the solution was carefully deoxygenated by applying a vacuum; hydrogen was admitted at this point to the desired pressure, the reactor was heated to the required temperature by circulating a thermostatted liquid through the jacket around the reactor, and magnetic stirring was immediately commenced. The reaction was followed by measuring the hydrogen pressure as a function of time. The conversion of reactants in the catalytic reactions was generally (although not necessarily) kept below 10% (*ca.* 5−20 turnovers) in order to use the initial rates method in our calculations. The measured $\Delta P(H_2)$ values were converted to millimoles of DHBT produced, and the data were plotted as molar concentration of the product as a function of time, yielding straight lines. Initial rates were then obtained from the corresponding slopes. All straight lines were fitted by use of conventional linear regression software to $r^2 > 0.98$. Concentrations of dissolved hydrogen were calculated using published solubility data.[8]

Table 1. Summary of Crystal Data for 3b

formula	$C_{52}H_{46}F_6Ir_1P_3S_2$
mw	1134.17
cryst size, mm	0.32 × 0.32 × 0.32
cryst syst	orthorhombic
space group	*Fdd*2 (No. 43)
a, Å	13.608(1)
b, Å	34.837(6)
c, Å	20.268(4)
V, Å^3	9608.29
Z	8
D_{calc}, g cm^{-3}	1.56
μ (Cu Kα), cm^{-1}	82.24
radiation	Mo Kα, $\lambda = 0.710\ 69$
scan type	ω
2θ range, deg	5−45
scan width, deg	$0.7 + 0.35 (\tan \theta)$
total data	2310
no. of unique data, $I \geq 3\sigma(I)$	1873
no. of parameters	162
R	0.0339
R_w	0.0363
abs corr min−max	0.94−1.00

Synthesis of $[Ir(H)_2(\eta^1(S)\text{-DHBT})_2(PPh_3)_2]PF_6$ (3b). To a solution of **1b** (200 mg, 0.21 mmol) in CH_2Cl_2 (20 mL) was added BT (170 mg, 1.26 mmol), and hydrogen was bubbled through the mixture for 1 h, during which the color of the solution changed from red to yellow. The solution was reduced to ca. $^1/_2$ of its initial volume and then precipitated under H_2 with diethyl ether; the solid was filtered off and dried in vacuo (75% yield; ^1H NMR (CD_2Cl_2, 298 K) δ 7.5−7.0 (m, PPh_3 and H_{4-7}-DHBT), 2.7−2.9 (m, H_2- and H_3-DHBT), −16.8 (t, J(HP) = 16.8 Hz, Ir−H); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K) δ 12.5 (s, PPh_3), −145 (sept, PF_6^-). Anal. Calcd for $C_{52}H_{46}F_6IrP_3S_2$: C, 55.07; H, 4.09; S, 5.66. Found: C, 54.92; H, 4.18; S, 5.73.

X-ray Diffraction Study. A summary of the crystal and intensity data for **3b** is reported in Table 1. The data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer. Unit-cell dimensions were determined from the least-squares refinement of the angular settings of 25 carefully centered reflections. Intensity data were corrected for Lorentz-polarization effects using the ψ-scan technique. Atomic scattering factors were taken from ref 9. The calculations were performed on a DIGITAL DEC 5000/200 computer, by using the SHELX76 program. The structure was solved by the heavy-atom technique. Both the metal complex cation and the PF_6^- anion have inner C_2 symmetry, with the Ir and the phosphorus atom of the counteranion lying on the 2-fold axis, coinciding with the lattice c axis. Refinement was done by full-matrix least-squares calculations initially with isotropic thermal parameters and then with anisotropic thermal parameters for Ir, S, and P atoms. Since no major peak attributable to the unique hydride ligand was detected in the ΔF Fourier maps (even at a later stage of refinement), this H ligand was successfully located by using the program HYDEX with an imposed Ir−H distance of 1.61 Å.[10] No attempt was made to refine this H atom. The hydrogen atoms linked to carbon atoms were introduced as usual at calculated positions (C−H = 1.08 Å). Because of the polarity of the *Fdd*2 space group, two possible enantiomeric structures must be considered (X, Y, Z and X, Y, $-Z$). The refinement of the model yielded $R = 0.0339$ and $R_w = 0.0363$, whereas the refinement

---

(5) Sánchez-Delgado, R. A.; Herrera, V.; Bianchini, C.; Masi, D; Mealli, C. *Inorg. Chem.* **1993**, *32*, 3766.

(6) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 2397. (b) Haines, L. M.; Singleton, E. *J. Chem. Soc. Dalton Trans.* **1972**, 1891. (c) Luo, X-L.; Schulte, G. K.; Crabtree, R. H. *Inorg. Chem.* **1990**, *29*, 682.

(7) Sánchez-Delgado, R. A.; Andriollo, A.; Puga, J.; Martín, G. *Inorg. Chem.* **1987**, *26*, 1867.

(8) *Solubility Data Series*; Young, C. L., Ed.; Pergamon: Oxford, 1981; Vol. 516, p 239.

(9) Cromer, D. T.; Waber, J. T. *Acta Crystallogr.* **1965**, *18*, 104.

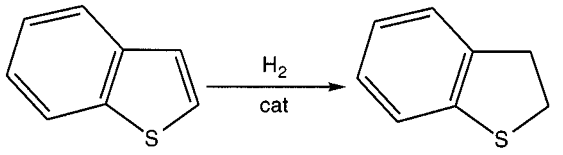
(10) Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1980**, 2509.

of the enantiomorph yielded $R = 0.0342$ and $R_w = 0.0368$. This excludes the latter choice.

Results and Discussion

In our previous work, we found that the rhodium complex **1a** displayed a rather low activity as a catalyst precursor for the hydrogenation of BT to DHBT in 2-methoxyethanol at 125 °C and subambient H_2 pressure.[3c] Under those conditions, the analogous iridium complex **1b** was inactive; however, a modest activity in THF under more stringent reaction conditions (170 °C, 110 bar of H_2) had been reported earlier.[3a]

Now we have found that both complexes **1a** and **1b** are extremely active catalysts for the specific hydrogenation of BT to DHBT (eq 1), if 1,2-dichloroethane is used as the solvent. This marked effect of the solvent on the rates of hydrogenation has important mechanistic implications that will be considered below. Due to the exceedingly high rates obtained in 1,2-dichloroethane, it became necessary to lower the reaction temperature to 40 °C, in order to achieve reasonable rates that allowed us to carry out kinetic measurements at ambient or subambient pressure.



(1)

We have previously noted that complexes **1a** and **1b** react rapidly with H_2 and BT to yield the corresponding dihydrides $[M(H)_2(\eta^1(S)\text{-BT})_2(PPh_3)_2]PF_6$ (M = Rh, **2a**; Ir, **2b**). Although **2a** proved to be too unstable to be properly identified, **2b** may be isolated in a pure form[5] and its use as the catalyst precursor is more convenient in the case of Ir.

Although all of the reaction mixtures had the appearance of homogeneous solutions with no evidence of metallic components, the homogeneity of the hydrogenation runs was further inferred from the high selectivity observed, together with an excellent reproducibility of the kinetic measurements, and from the fact that the addition of mercury to the solutions did not affect the catalytic rates.[11]

Kinetics of BT Hydrogenation. The kinetics of the hydrogenation of BT to DHBT in 1,2-dichloroethane solution were studied by carrying out runs at different catalyst, substrate, and hydrogen concentrations and at different temperatures for each catalyst precursor. The complete data are listed in Tables 2 and 3 for **1a** and **2b**, respectively.

The initial rates (r_i) showed a direct dependence with respect to the catalyst concentration, as confirmed by plots of log r_i *vs* log [cat] which yielded straight lines with slopes of 1.0 for **1a** and 1.1 for **2b**. No effect on the hydrogenation rates was observed on varying the substrate concentration. The variation of the initial rates with hydrogen concentration indicates a first-order dependence with respect to hydrogen at low pressures, which tends toward zero order at concentrations above 2.4×10^{-5} M. A first-order dependence was confirmed in the low-pressure regime by the slope values of the plots of log r_i *vs* log $[H_2]$ (0.9 for **1a** and 1.0 for **2b**).

Table 2. Kinetic Data for the Hydrogenation of Benzothiophene, Using 1a as the Catalyst Precursor[a]

10^4 [Rh], M	10^2 [BT], M	10^5 [H_2], M	T, °C	$10^6 r_i$, M s^{-1}	k_{cat}, M^{-1} s^{-1}
5.0	5.0	2.4	40	1.5	125
6.6	5.0	2.4	40	2.0	126
8.0	5.0	2.4	40	2.4	125
10.0	5.0	2.4	40	2.8	117
12.0	5.0	2.4	40	3.6	125
8.0	2.5	2.4	40	2.6	135
8.0	7.5	2.4	40	2.2	115
8.0	10.0	2.4	40	2.4	125
8.0	5.0	1.2	40	1.3	135
8.0	5.0	1.5	40	1.9	158
8.0	5.0	1.8	40	2.1	145
8.0	5.0	2.0	40	2.2	138
8.0	5.0	2.1	40	2.3	137
8.0	5.0	2.4	20	2.0	104
8.0	5.0	2.4	30	2.2	115
8.0	5.0	2.4	50	3.6	187

[a] Solvent: 1,2-dichloroethane (100 mL); r_i = initial rates.

Table 3. Kinetic Data for the Hydrogenation of Benzothiophene, Using 2b as the Catalyst Precursor[a]

10^4 [Ir], M	10^2 [BT], M	10^5 [H_2], M	T, °C	$10^6 r_i$, M s^{-1}	k_{cat}, M^{-1} s^{-1}
5.0	5.0	2.2	40	5.1	464
6.6	5.0	2.2	40	7.6	523
8.0	5.0	2.2	40	9.2	523
10.0	5.0	2.2	40	12.1	550
12.0	5.0	2.2	40	12.5	473
8.0	2.5	2.2	40	10.9	619
8.0	7.5	2.2	40	10.3	585
8.0	10.0	2.2	40	11.5	653
8.0	5.0	1.5	40	6.3	525
8.0	5.0	1.8	40	6.9	479
8.0	5.0	2.0	40	8.0	500
8.0	5.0	2.1	40	8.5	506
8.0	5.0	2.4	40	9.5	495
8.0	5.0	2.2	20	5.5	313
8.0	5.0	2.2	30	8.0	455
8.0	5.0	2.2	50	14.2	807

[a] Solvent: 1,2-dichloroethane (100 mL); r_i = initial rates.

Consequently, the experimental rate law can be written as

$$d[DHBT]/dt = k_{cat}[M][H_2] \tag{2}$$

The average values for the catalytic rate constants at 313 K as well as their standard errors ($\sigma/(n)^{1/2}$) were calculated from eq 2, using the data shown in Table 2, $k_{cat(Rh)} = (131 \pm 3)$ M^{-1} s^{-1}, and in Table 3, $k_{cat(Ir)} = (530 \pm 16)$ M^{-1} s^{-1}. The fact that the rate law found for the rhodium and iridium complexes in 1,2-dichloroethane (eq 2) is identical to the one previously determined for the same rhodium system in 2-methoxyethanol[3c] indicates that the mechanisms for both precatalysts in the two solvents are closely related.

The effect of the temperature on the rate constants was studied in the range 293−323 K for [BT] = 5.0×10^{-2} M, [catalyst] = 8.0×10^{-4} M, and [H_2] = 2.4×10^{-5} M (Rh) and 2.2×10^{-5} M (Ir). Within the range of conditions used, the variation of the solubility of hydrogen with temperature is negligible. Plots of ln k_{cat} vs $1/T$ allowed us to evaluate the activation energy E_a, the

---

[11] (a) Crabtree, R.; Anton, D. R. *Organometallics* **1983**, *2*, 855. (b) Whitesides, G. M.; Hacket, M.; Brainard, R. L.; Lavalleye, J.-P. P. M.; Sowinski, A. F.; Izumi, A. N.; Moore, S. S.; Brawn, D. W.; Staudt, E. M. *Organometallics* **1985**, *4*, 1819.

Table 4. Activation Parameters for the Hydrogenation of Benzothiophene Catalyzed by Rhodium and Iridium Complexes

parameter	$[Rh(COD)(PPh_3)_2]PF_6$ (**1a**)	$[Ir(H)_2(BT)_2(PPh_3)_2]PF_6$ (**2b**)
E_a, (kcal/mol)	3.5 ± 0.5	5.7 ± 0.5
A, $M^{-1}\ s^{-1}$	$(4.2 \pm 0.5) \times 10^4$	$(5.3 \pm 0.5) \times 10^6$
k_{cat} (25 °C), $M^{-1}\ s^{-1}$	1.09×10^2	3.68×10^2
$\Delta H^{\ddagger}$, kcal/mol	2.9 ± 0.4	5.1 ± 0.6
$\Delta S^{\ddagger}$, eu	-41.3 ± 0.8	-31.7 ± 0.8
$\Delta G^{\ddagger}$, kcal/mol	16 ± 3	15 ± 3

frequency factor A, the extrapolated value of the rate constant at 298 K, and the values of enthalpy, entropy, and free energy of activation (calculated from the equations $\Delta H^{\ddagger} = E_a - RT$; $\Delta S^{\ddagger} = R\ \ln(hA/e^2k_BT)$ and $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$, respectively); these data are listed in Table 4.

It is important to note at this point that if the values of k_{cat} (298 K) are taken as a measure of the catalytic efficiency, the Ir system ($k_{cat} = 3.68 \times 10^2\ M^{-1}\ s^{-1}$) turns out to be about 3 times more active than the Rh analog ($k_{cat} = 1.09 \times 10^2\ M^{-1}\ s^{-1}$). Also, the Rh catalyst is surprisingly about 10^6 times faster in 1,2-dichloroethane than in 2-methoxyethanol (k_{cat} (298 K) $= 1.24 \times 10^{-4}$ $M^{-1}\ s^{-1}$);[3c] correspondingly, the free energies of activation for the hydrogenation of BT in 1,2-dichloroethane (16 kcal/mol for Rh and 15 kcal/mol for Ir) are considerably smaller than that found for the same rhodium catalyst in 2-methoxyethanol (23 kcal/mol). These trends will be discussed below in relation to the proposed hydrogenation mechanism.

Synthesis and X-ray Structure of $[Ir(H)_2(\eta^1(S)\text{-}DHBT)_2(PPh_3)_2]PF_6$ (3b). As mentioned above, one of the problems encountered in our earlier mechanistic studies with Rh catalysts was the instability of the active intermediates, which did not allow us to isolate or directly observe many of the important species implicated in the cycle; this led us to carry out some interesting theoretical calculations that complemented our kinetic work and offered additional support for our proposed catalytic cycle.[3b,c] Our previous work on Ir catalysis in THF was carried out under severe conditions, which precluded any attempts to elucidate the reaction mechanism.[3a]

Moving to iridium chemistry in chlorinated solvents opened the possibility not only of obtaining highly active catalysts, but also of isolating and characterizing some of the key species involved in the catalysis. We have reported that bubbling hydrogen through a solution of **1b** in the presence of excess BT rapidly leads to the quantitative formation of the species representing the starting point of the catalytic cycle, **2b** (eq 3); this is a

$$\underset{\textbf{1b}}{[Ir(COD)(PPh_3)_2]PF_6} + H_2 + 2BT \rightarrow \underset{\textbf{2b}}{[Ir(H)_2(\eta^1(S)\text{-}BT)_2(PPh_3)_2]PF_6} \quad (3)$$

rather stable compound amenable to analytical and spectroscopic characterization.[5]

If the interaction with hydrogen is allowed to proceed for a longer time (1 h), a new stable product can be isolated in high yields as a white solid. The ^1H NMR spectrum of the new complex displays, besides a complex pattern of signals in the aromatic region, a multiplet signal between 2.7 and 2.9 ppm assigned to H(2) and H(3) of the hydrogenated substrate, DHBT, plus a high-field triplet at −16.8 ppm, ^2J (HP) = 16.8 Hz, due to the metal hydrides; the $^{31}P\{^1H\}$ NMR spectrum consists of a singlet at 12.5 ppm, besides the PF_6^- signal. These data are in very good agreement with those reported for other related complexes $[Ir(H)_2(\eta^1(S)\text{-}Th)_2\text{-}(PPh_3)_2]PF_6$ complexes previously prepared and fully characterized by us (Th = thiophene, tetrahydrothiophene, dibenzothiophene).[5] Therefore, we can conclude that the new complex is $[Ir(H)_2(\eta^1(S)\text{-}DHBT)_2\text{-}(PPh_3)_2]PF_6$ (**3b**).

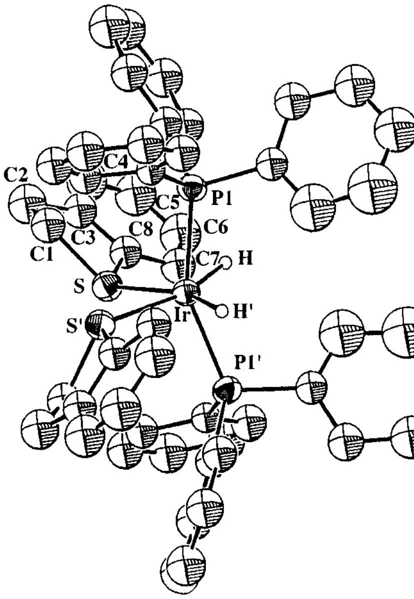


Figure 1. ORTEP drawing of the cation $[Ir(H)_2(\eta^1(S)\text{-}DHBT)_2(PPh_3)_2]^+$.

An X-ray diffraction study confirmed this formulation. Figure 1 shows an ORTEP representation of the complex cation. Selected bond distances and angles are collected in Table 5. The coordination geometry around the metal atom consists of a distorted octahedron with *cis* sulfur atoms, *cis* hydrides, and *trans* phosphines. The main distortion from the ideal octahedral geometry is the bending of the bulky phosphine ligands toward the small hydrides, in order to minimize steric repulsions. The Ir−S distance (2.420 Å) is shorter than those found in the analogous iridium complexes with thiophene (2.452 Å) and tetrahydrothiophene (2.457 Å)[5] and somewhat longer than those found in other η^1-S-bonded metal complexes of thiophenes, $Cp^*(CO)_2Re(T)$ (2.360 Å),[12a] $Cp^*(CO)_2Re(3\text{-}MeBT)$ (2.356 Å),[12b] $[Cp(CO)(PPh_3)\text{-}Ru(2\text{-}Me\text{-}T)]BF_4$ (2.392 Å),[13] $CpFe(CO)_2(\eta^1S\text{-}DBT)$ (2.289 Å),[14] $Cp^*IrCl_2(DBT)$ (2.375 Å),[15] $[(PPh_3)_2Ru(C_5H_4\text{-}$

---

[12] (a) Choi, M. G.; Angelici, R. J. *Organometallics* **1991**, *10*, 2436. (b) Choi, M. G.; Angelici, R. J. *Organometallics* **1992**, *11*, 3328.

[13] Benson, J. W.; Angelici, R. J. *Organometallics* **1992**, *11*, 922.

[14] Goodrich, J. D.; Nickias, P. N.; Selegue, J. P. *Inorg. Chem.* **1987**, *26*, 3424.

[15] Mohan Rao, K.; Day, K. L.; Jacobson, R. A.; Angelici, R. J. *Inorg. Chem.* **1991**, *30*, 5046.

Table 5. Selected Bond Distances (Å) and Angles (deg) for 3b

Distances			
Ir−P$_1$	2.319(2)	C$_3$−C$_4$	1.37(2)
Ir−H	1.609	C$_3$−C$_8$	1.37(2)
Ir−S	2.420(3)	C$_4$−C$_5$	1.34(2)
S−C$_1$	1.83(1)	C$_5$−C$_6$	1.34(2)
S−C$_8$	1.77(1)	C$_6$−C$_7$	1.39(2)
C$_1$−C$_2$	1.48(2)	C$_7$−C$_8$	1.40(2)
C$_2$−C$_3$	1.50(2)		
Angles			
S−Ir−P$_1$	95.2	S−C$_1$−C$_2$	105.4(1)
S−Ir−P$_1$′	102.9(1)	C$_1$−C$_2$−C$_3$	108.9(1)
H−Ir−S	79.0	C$_2$−C$_3$−C$_4$	127.7(1)
S′−Ir−H	161.5(1)	C$_2$−C$_3$−C$_8$	113.8(1)
H−Ir−P$_1$	82.3(1)	C$_4$−C$_3$−C$_8$	118.5(1)
H−Ir−P$_1$′	84.9(1)	C$_3$−C$_4$−C$_5$	120.4(2)
P$_1$−Ir−P$_1$′	154.7(1)	C$_4$−C$_5$−C$_6$	120.7(2)
S−Ir−S′	83.4(1)	C$_5$−C$_6$−C$_7$	123.1(1)
H−Ir−H′	119.0	C$_6$−C$_7$−C$_8$	114.4(1)
Ir−S−C$_1$	114.2	S−C$_8$−C$_7$	125.9(1)
Ir−S−C$_8$	119.6	S−C$_8$−C$_3$	111.4(1)
C$_1$−S−C$_8$	91.8(1)	C$_3$−C$_8$−C$_7$	122.8(1)

$CH_2C_4H_3S)]^+$ (2.408 Å),[16] and $[Cp(PMe_3)Ru(2,5\text{-DHT})]^+$ (2.330 Å).[17] The sulfur atom adopts a pyramidal geometry corresponding to an approximate sp^3 hybridization; correspondingly, the sum of the angles around the S atom (326°) is much less than the 360° required for a trigonal planar disposition. All of the other structurally characterized η^1-S-thiophene complexes[5,11−16] also contain pyramidal S atoms, although minor geometrical differences are observed from one complex to another. This type of geometry around the sulfur in metal thiophene complexes has been properly accounted for by use of theoretical arguments.[18] As expected, the C$_1$−C$_2$ and C$_2$−C$_3$ distances (1.48 and 1.50 Å), as well as the S−C$_1$−C$_2$ and C$_1$−C$_2$−C$_3$ angles (105.4° and 108.9°) are in agreement with sp^3-hybridized carbon atoms of the hydrogenated ring; all other distances and angles in the DHBT and PPh$_3$ ligands may be considered normal.

With regard to the catalysis, it is important to note that complex **3b** does not react with excess BT in boiling 1,2-dichloroethane and it is completely inactive as a catalyst precursor for BT hydrogenation under the conditions described above for **1a** and **2b**.

The Mechanism of BT Hydrogenation. On the basis of the results presented above, we propose that complex **1a** reacts with H$_2$ and BT to yield the dihydrido species **2a**, analogous to the isolated Ir complex **2b**. From this point onward the cycles for both metals proceed in the same way; and therefore, they will be discussed in a generic manner. Although we have not been able to obtain direct experimental evidence for the the formation of electronically unsaturated mono-BT intermediates, our previous theoretical analysis[3c] indicates that complex **2** loses a BT molecule to yield the 16-electron species $[M(H)_2(BT)(PPh_3)_2]^+$ (**4**), probably as an equilibrium mixture of η^1-(S)- and η^2-(C=C)-forms.[12b,18] Hydrogen transfer to the remaining coordinated BT produces the intermediate $[M(DHBT)(PPh_3)_2]^+$ (**5**), according to eq 4. Subsequent displacement of the DHBT ligand in **5** by a new BT molecule

$$\underset{\mathbf{4}}{[M(H)_2(BT)(PPh_3)_2]^+} \xrightarrow[\text{rds}]{k_1} \underset{\mathbf{5}}{[M(DHBT)(PPh_3)_2]^+} \quad (4)$$

$$\underset{\mathbf{5}}{[M(DHBT)(PPh_3)_2]^+} + BT \xrightarrow{k_2} \underset{\mathbf{6}}{[M(BT)(PPh_3)_2]^+} + DHBT \quad (5)$$

$$\underset{\mathbf{6}}{[M(BT)(PPh_3)_2]^+} + H_2 \overset{K_3}{\rightleftharpoons} \underset{\mathbf{4}}{[M(H)_2(BT)(PPh_3)_2]^+} \quad (6)$$

yields $[M(BT)(PPh_3)_2]^+$ (**6**), and the catalytic cycle is completed by the reaction of **6** with hydrogen to yield the dihydrido species **4**, according to the equilibrium represented by eq 6.

If the rate determining step is the intramolecular hydrogenation of coordinated BT, represented by eq 4, a rate law can be derived as follows:

$$r_i = k_1[\mathbf{4}] \quad (7)$$

Taking into account the equilibrium in eq 6 ($[\mathbf{4}] = K_3[\mathbf{6}][H_2]$), we have

$$r_i = k_1K_3[\mathbf{6}][H_2] \quad (8)$$

Assuming that **5** is rapidly transformed to **6,** the mass balance for the metal is $[M]_0 = [\mathbf{4}] + [\mathbf{6}]$; and therefore, the concentration of **6** may be expressed as:

$$[\mathbf{6}] = \frac{[M]_0}{1 + K_3[H_2]} \quad (9)$$

Substituting [**6**] in eq 8 allows us to rewrite the rate expression as

$$r_i = \frac{k_1K_3}{1 + K_3[H_2]}[M]_0[H_2] \quad (10)$$

This theoretical rate law is in good accord with our experimental findings in that it explains why the dependence of the reaction rate with respect to hydrogen concentration tends to change from first to zero order on going from low to high hydrogen pressures. Provided that the hydrogen concentration in solution is small (as in our reaction conditions), the term $K_3[H_2] \ll 1$ and the rate expression can be reduced to

$$r_i = k_1K_3[M]_o[H_2] \quad (11)$$

which is identical to our experimentally determined rate expression, where $k_{cat} = k_1K_3$.

Conclusions

Our experimental findings allow us to postulate the catalytic cycle represented in Scheme 1. The species within the dotted lines are the ones we believe to be directly participating in the hydrogenation catalysis. BT initially binds η^1-S to a M(III) dihydride (M = Ir, Rh); dissociation of a BT molecule yields species **4**, which is very likely in equilibrium with the isomeric dihydrido−η^2-BT complex. This olefin-like intermediate undergoes stepwise selective hydrogenation of the C$_2$=C$_3$ bond, through a hydridodihydrobenzothienyl species, to yield intermediates containing the hydrogenated product $[M(\eta^1(S)\text{-DHBT})(PPh_3)_2]^+$ (**5**). The hydride migration

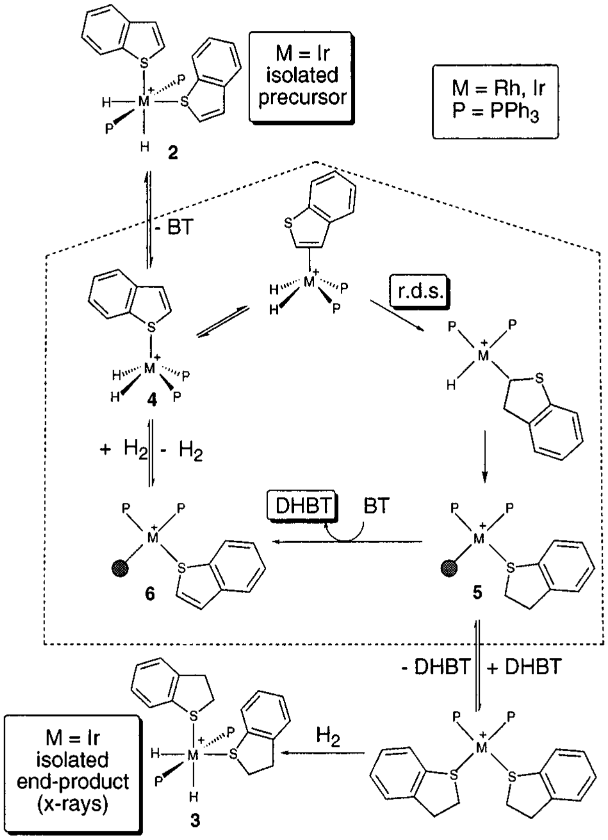
---

(16) Draganjac, M.; Rauchfuss, T. B.; Ruffing, C. J. *Organometallics* **1985**, *4*, 1909.

(17) Sutherland, H. H.; Rawas, A. *Acta Crystallogr.* **1985**, *C41*, 929.

(18) Rincón, L.; Terra, J.; Guenzburger, D.; Sánchez-Delgado, R. A. *Organometallics* **1995**, *14*, 1292.

Scheme 1. Postulated Mechanism for the Hydrogenation of Benzothiophene by Use of $[M(H)_2(\eta^1(S)\text{-BT})_2(PPh_3)_2]PF_6$ (M = Rh, Ir) as the Catalyst Precursors



intermediate may be a 2-benzothienyl or a 3-benzothienyl complex. In the absence of any experimental evidence to favor one of these species, we suggest that migration of the hydride occurs to the 3-position on the following basis: (i) our previous CNDO calculations[3c] indicate that the C(2) atom of free BT has a greater negative charge than the C(3) atom, and that for the Rh catalyst, the 2-benzothienyl intermediate is energetically slighly favored over the 3-benzothienyl species; (ii) more recent ab initio studies on the free BT molecule[19] also indicate that C_α is more negatively charged than C_β and thus more susceptible to electrophilic attack. Displacement of DHBT of **5** by a new molecule of BT produces $[M(\eta^1(S)\text{-BT})(PPh_3)_2]^+$ (**6**), which reacts with hydrogen to produce **4** and restart the cycle.

The outer species do not participate directly in the catalysis, and an accumulation of any one of them should result in loss of activity. Indeed, this is what happens as the catalytic reaction progresses in the case of Ir; as DHBT accumulates, **5b** is in equilibrium with the bis(DHBT) complex $[Ir(DHBT)_2(PPh_3)_2]^+$, which in turn can react irreversibly with H_2 to favor the formation of **3b**, a stable species which is not active in catalysis. As a consequence, the system gradually loses its activity and complex **3b** can be isolated from the reaction medium as a pure crystalline material which was shown to be inert toward excess BT and inactive as a catalyst precursor.

An alternative pathway that needs to be considered in our reaction conditions is the addition of BT to complex **5** under H_2 to yield $[M(\eta^1(S)\text{-BT})(DHBT)(PPh_3)_2]^+$ and/or $[M(H)_2(\eta^1(S)\text{-BT})(DHBT)(PPh_3)_2]^+$. Although we have not been able to detect such mixed BT/DHBT intermediates, they are likely to be implicated in the catalyst deactivation processes rather than in the actual catalytic cycle; our previous theoretical work[3c] indicated that η^2-(C=C)−BT coordination (necessary for the hydrogenation reaction to take place) in a bis−(BT) complex would be energetically unfavored for steric reasons, and a mixed BT/DHBT intermediate would be even more crowded.

This general catalytic cycle is rather similar to the one previously postulated for the rhodium system in 2-methoxyethanol;[3c] in both cases, we go through the cycle using only M(I)/M(III) (M = Rh, Ir) couples formed by standard oxidative-addition−reductive-elimination processes. The presence of various coordinatively unsaturated species within the kinetically important catalytic cycle allows us to understand the marked effect of the solvent found in our systems; in a coordinating solvent such as 2-methoxyethanol, these unsaturated species are probably sufficiently stabilized through solvation for the catalysis to be retarded (Rh) or inhibited (Ir), as a result of an efficient competition of the solvent with the BT substrate for the vacant coordination sites. Similar considerations may be applied in the case of the slow Ir-catalyzed hydrogenation in THF, also a strongly coordinating solvent. On the other hand, 1,2-dichloroethane coordinates poorly to Rh or Ir and thus favors higher concentrations of the reactive (unsolvated) unsaturated intermediates, which may then bind BT (also a poor ligand) effectively, resulting in the much higher catalytic rates observed in this latter solvent. The fact that the M−S and M(C=C) bonds needed in **4** and its η^2-(C=C) isomer are generally stronger for Ir than for Rh may also provide an explanation for the unusual observation of somewhat higher activities for the third-row metal complex as compared with its second-row analog.

As in the cycle previously proposed for Rh,[3c] we favor the involvement of the η^2-bonding mode in the hydrogenation of benzothiophene. Other workers have demonstrated the importance of η^2-coordination in the activation of thiophenes.[12b,20] An important advance with respect to our previous work is the identification of the outer species $[Ir(H)_2(\eta^1(S)\text{-BT})_2(PPh_3)_2]PF_6$, which represents the entry into the cycle, and $[Ir(H)_2(\eta^1(S)\text{-DHBT})_2(PPh_3)_2]PF_6$, the end point of the catalysis, formed as a consequence of the strong binding of DHBT to Ir(III). We have not been able to observe the analogous Rh BT and DHBT complexes, since the catalytic solutions decompose rapidly at the end of the runs with the Rh catalyst, but all of the accumulated data indicate that the hydrogenation mechanism is the same for both metals.

Another important difference with respect to the mechanism previously described by us for Rh is the absence of η^5-bonded BT complexes in the new general cycle described in Scheme 1. We believe that in the rhodium system, the species **6** with one $\eta^1(S)$-BT may be in equilibrium with an η^5-intermediate $[Rh(\eta^5\text{-BT})$-

---

(19) Hinchliffe, A.; Soscún Machado, H. J. *J. Mol. Struct. (Theochem)* **1995**, *334*, 235.

(20) Choi, M.-G.; Robertson, M. J.; Angelici, R. J. *J. Am. Chem. Soc.* **1991**, *113*, 4005.

$(PPh_3)_2]PF_6$, closely related to the only structurally characterized η^5-thiophene complex, $[Rh(\eta^5\text{-T})(PPh_3)_2]PF_6$, which some of us synthesized in 1986 by reaction of $[Rh(COD)(PPh_3)_2]PF_6$ with thiophene and H_2, probably through an unstable intermediate analogous to **2a**;[21] some NMR evidence, as well as theoretical calculations, supported this idea. The reversible reaction of $[Rh(\eta^5\text{-BT})(PPh_3)_2]^+$ with H_2 to form $[Rh(H)_2(\eta^2\text{-BT})(PPh_3)_2]$ was taken as a possible key step in the catalytic cycle; however, the alternative pathway available, involving only η^1- and η^2-bonded BT, was also noted.

In the case of Ir, we have not found any evidence for this η^5-binding form and it is likely that in the case of Rh, even if such a species is formed, its participation in the catalysis is minor, and thus the major catalytic cycle proceeds in the way described by Scheme 1 for both Rh and Ir in 1,2-dichloroethane or 2-methoxyethanol.

Acknowledgment. We thank CONICIT for generous financial support to V.H. (Project S1-95000693), CONICIT and CNR for an International Cooperation Grant to R.A.S.-D. and C.B., and La Universidad del Zulia (LUZ) for a Doctoral Fellowship and leave of absence to M.R. Thanks are due to Mr. Dante Masi for the X-ray crystal structure determination.

Supporting Information Available: Atomic parameters (Table S1) and coordinates of hydrogen atoms (Table S2) for **3b** (2 pages). Ordering information is given on any current masthead page.

OM961007L

---

[21] Sánchez-Delgado, R. A.; Márquez-Silva, R.-L.; Puga, J.; Tiripicchio, A.; Tiripicchio-Camellini, M. *J. Organomet. Chem.* **1986**, *316*, C35.