ORGANOMETALLICS
Organometallics, 1996, 15(12), 2678-2679, DOI:10.1021/om9601615

Supporting Information

Tp*Rh(C_2H_4)(PMe_3) **1a**

A stirred solution of Tp*Rh(C_2H_4)$_2$ (0.81 g, 1.75 mmol) in THF (40 ml) is cooled to -30 °C and PMe_3 is added (1.75 ml of a solution 1M in THF, 1.75 mmol). The initial orange color of the solution becomes pale yellow. After stirring for 15 min. at -30 °C, the solution is warmed to room temperature and stirred during 1 h, after which time the solvent is removed in vacuo, yielding a microcrystalline solid. The NMR spectra of the solid obtained reveals quantitative formation of **1a**, pure enough for preparative purposes. The high sensitivity of this complex to oxygen, coupled with its high solubility in organic solvents prevents its recrystallization and, hence, the elemental analysis determination.

Tp*Rh(H)(2-C_4H_3S)(PMe_3) **2a**

0.05 g of **1a** (0.1 mmol) are dissolved in thiophene (30 ml) and heated at 90 °C during 6h. The yellow solution changes to brown-orange. The thiophene is evaporated under reduced pressure and a brown solid is obtained which contains, as revealed by NMR, 85 % of the title compound, together with small amounts of the isomer Tp*Rh(CHCHCHCHS)(PMe_3). Extraction with petroleum ether gives a solution enriched in complex **2a**, although complete separation upon crystallization could not be achieved.

Tp*Rh(CHCHCHCHS)(PMe_3) **3a**

Complex **1a** (0.23 g, 0.45 mmol) is dissolved in thiophene (50 ml) and transferred to a photorreactor. The mixture is then irradiated, at room

temperature, for 2 h and the resulting orange solution is evaporated to dryness. NMR monitoring of the crude solid obtained reveals the presence of three species: complex **3a** (60 %), complex **2a** (20 %) and another unidentified species (20 %). Extraction of the mixture with petroleum ether (*ca* 2 x 10 ml) leaves **3a** as a solid, which can be crystallized from THF. Anal. Calcd.: C, 47.16; H, 6.30; N, 15.00. Found: C, 47.16; H, 5.96; N, 14.84.

Complexes **1b-3b** are prepared following procedures analogous than described for **1a-3a.**