C−H and C−S Activation of Thiophene by Rhodium Complexes: Influence of the Ancillary Ligands on the Thermodynamic Stability of the Products

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*Summary: The reaction of thiophene with the rhodium compound [Tp*Rh(C$_2$H$_4$)(PMe$_3$)] (**1a**; Tp* = hydrotris-(3,5-dimethyl-1-pyrazolyl)borate) leads to a mixture of the C−H and C−S activation products [Tp*Rh(H)(2-C$_4$H$_3$S)(PMe$_3$)] (**2a**) and [Tp*Rh(CHCHCHCHS)(PMe$_3$)] (**3a**), respectively. In contrast to previous observations, the former is the thermodynamically preferred isomer. For the PEt$_3$ derivative [Tp*Rh(C$_2$H$_4$)(PEt$_3$)] (**1b**), an even higher selectivity toward C−H activation is observed.*

Many synthetic and reactivity studies on model complexes that contain coordinated or chemically transformed thiophenes have been undertaken in recent years with the aim of gaining valuable information on the mechanism of the hydrodesulfurization reaction.[1,2] While thiophenes can be activated by different metals,[1,3] unusual and very often unexpected reactivity patterns have emerged from the use of Rh and Ir complexes of cyclopentadienyl[4] and other ligands.[5] Thienyl derivatives resulting from C−H activation[6] at the α-position of the thiophene ring, as well as products derived from C−S bond scission, are thought to be key intermediates in the process of sulfur removal.

Recent work points out that the σ-2-thienyl systems constitute an opening entry to the C−S insertion products. This is suggested by the observation of only C−S bond cleavage in a number of reactions of this type[7] and above all by the irreversible conversion of some σ-2-thienyls into the corresponding metallacyclic products.[4c,8] Here we wish to communicate that the unsaturated Tp*Rh(PMe$_3$) fragment (Tp* = hydrotris(3,5-dimethyl-1-pyrazolyl)borate) reverses the order of thermodynamic stability to favor the C−H oxidative-addition product [Tp*Rh(H)(2-C$_4$H$_3$S)(PMe$_3$)] (**2a**) *versus* the heterometallacycle [Tp*Rh(CHCHCHCHS)(PMe$_3$)] (**3a**). Moreover, a substantial increase of the selectivity of this transformation can be brought about by use of the PEt$_3$ derivative, which yields predominantly (>95%) the thienyl derivative **2b**.

Low-temperature (−20 °C) addition of 1 equiv of PMe$_3$ to solutions of [Tp*Rh(C$_2$H$_4$)$_2$][9] allows the isolation of the phosphine adduct **1a** in almost quantitative yield (eq 1). This mixed phosphine−ethylene derivative is a

$$[Tp^*Rh(C_2H_4)_2] + PMe_3 \longrightarrow \underset{\mathbf{1a}}{[Tp^*Rh(C_2H_4)(PMe_3)]} + C_2H_4 \quad (1)$$

yellow microcrystalline solid which can be readily identified by spectroscopy.[10] A characteristic feature is the observation of a $^{31}P\{^1H\}$ NMR doublet at δ 14.6 ($^1J_{P-Rh}$ = 152 Hz).

Irradiation of a solution of **1a** in neat thiophene for 3 h furnishes an orange solution which is shown by NMR to contain complexes **2a** and **3a** in a *ca.* 1:3 ratio (Scheme 1), together with a third, minor (<20%), unidentified species. Fractional crystallization from ether/petroleum ether mixtures permits the isolation of pure **3a**. Strong support for the formulation of this complex as the C−S insertion adduct can be gained from NMR studies.[11] The observation of thiophene-derived multiplets at δ 8.01 (1 H), 6.42 (2 H), and 6.16 (1 H) in the ^1H NMR spectrum and of $^{13}C\{^1H\}$ methyne signals at δ 121.1, 125.3, 126.4, and 143.2 (dd, $^1J_{C-Rh}$ or $^2J_{C-P}$ = 16 or 27 Hz) argues in favor of a localized metallacyclic structure[12] of the kind shown in Scheme 1.

NMR monitoring of the photolysis reaction reveals **2a** and **3a** are maintained in about the same ratio through-

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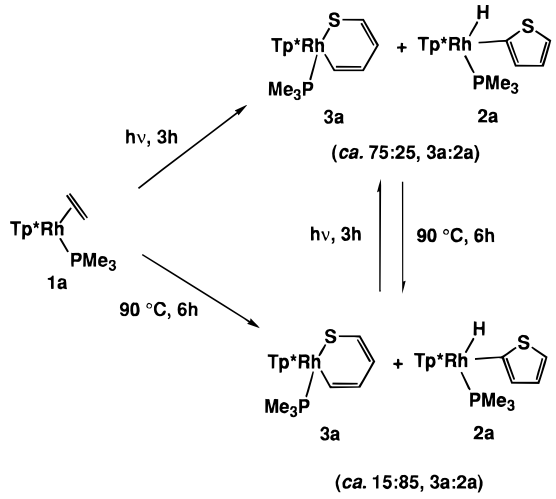
(10) Selected NMR data for **1a**: ^1H NMR (C_6D_6) δ 0.60 (d, 9 H, $^2J_{H-P}$ = 9.6 Hz, PMe$_3$), 1.87, 3.29 (very br s, 2 H, 2 H, C$_2$H$_4$), 2.08, 2.17, 2.41, and 2.45 (s, 3, 3, 6, 6 H, 6 Me), 5.19 (s, 1 H, CH), 5.83 (s, 2 H, 2 CH); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 11.8, 12.6, 13.2, 16.3 (s, 1:2:1:2 ratio, 6 Me), 14.7 (d, $^1J_{C-P}$ = 31 Hz, PMe$_3$), 16.3 (dd, J_{C-Rh} or J_{C-P} = 5 or 17 Hz, C$_2$H$_4$), 105.6, 106.9 (s, 2:1 ratio, 3 CH), 142.1, 144.3, 150.6, 150.7 (s, 1:2:1:2 ratio, 6 C$_q$); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 14.6 (d, $^1J_{Rh-P}$ = 152 Hz).

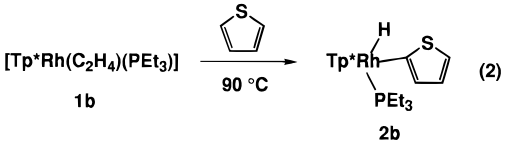
Scheme 1[a]



[a] All reactions conducted in neat thiophene.

out the irradiation period. Either pure complex **3a**, or alternatively the photolysis mixture, remain practically unaltered in solution upon standing at 20 °C. At higher temperatures (≥60 °C), however, the proportion of **2a** to **3a** in thiophene solution gradually changes to a final value of *ca*. 5.6:1. This same ratio is achieved when complex **1a** is heated at 90 °C in thiophene for 6 h. Pure crystalline **2a** can be separated from this mixture by crystallization and characterized by NMR.[11] Due to restricted rotation around the Rh−C bond, the proton resonances associated with the Tp*, PMe_3, and 2-C_4H_3S ligands are broad at room temperature, although they become sharper at 60 °C. The observation of a high-field ^{1}H resonance (δ −16.55, dd, $^1J_{H-Rh}$ = 22.6, $^2J_{H-P}$ = 31.1 Hz) is in accord with formulation of this compound as the C−H bond oxidative-addition adduct. In good agreement with other C−H activation reactions of thiophene which have been reported in the literature, only the 2-thienyl derivative seems to form.

The related [Tp*Rh(C_2H_4)(PEt_3)] species **1b**, which can be prepared similarly to **1a**, provides upon photolysis at either 0 or 20 °C a *ca*. 1:1 mixture of the C−H and C−S activation complexes **2b** and **3b**, respectively, again accompanied by 20−30% of an unidentified species. Interestingly, increased selectivity toward C−H bond rupture is observed during the thermal activation of **1b** (eq 2), the hydrido 2-thienyl product **2b** being



formed almost exclusively (>95%) upon heating a solution of **1b** in thiophene at 90 °C. Heating the photolysis mixture of **2b** and **3b** gives similar results.

In summary, it has been shown for the first time that the relative thermodynamic stability of the C−H and C−S bond activation products of thiophene by transition-metal complexes depends drastically upon the nature of the ancillary ligands. Thus, while in the system derived from the Cp*RhL metal fragments (L = PMe_3,[4c,d] C_2H_4[4e]) the C−S oxidative-addition products are preferred, for the somewhat similar Tp*Rh(PMe_3) moiety the C−H activation product clearly predominates. The observation of even higher selectivity for the Tp*Rh(PEt_3) unit seems to suggest that appropriate tuning of the electronic and steric properties of the metal environment may drive the reaction toward one or the other type of product in other metal systems. Part of our present efforts in this area of research are directed toward ascertaining the veracity of this assumption.

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Supporting Information Available: Text giving experimental details for the syntheses of compounds **1**−**3** and analytical data (2 pages). Ordering information is given on any current masthead page.

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(11) Selected NMR data for **2a**: ^{1}H NMR (C_6D_6, 70 °C) δ −16.55 (dd, 1 H, $^1J_{H-Rh}$ = 22.6, $^2J_{H-P}$ = 31.1 Hz, Rh−H), 1.24 (d, 9 H, $^2J_{H-P}$ = 9.5 Hz, PMe_3), 1.76, 2.14, 2.16, 2.18, 2.27, 2.39 (s, 3, 3, 3, 3, 3, 3 H, 6 Me), 5.44, 5.61, 5.82 (s, 1, 1, 1 H, 3 CH(Tp*)), 6.66 (br d, 1 H, $^3J_{H-P}$ = 2.5 Hz, CH), 6.98 (br dd, 1 H, $^3J_{H-H}$ = 3.2, 5.1 Hz, CH), 7.31 (d, 1 H, $^3J_{H-P}$ = 5.1 Hz, CH); ^{31}P{^{1}H} NMR (C_6D_6) δ 1.2 (br d, $^1J_{P-Rh}$ = 146 Hz). Selected NMR data for **3a**: ^{1}H NMR (C_6D_6) δ 1.17 (d, 9 H, $^2J_{H-P}$ = 9.9 Hz, PMe_3), 2.10 (s, 3 H, Me), 2.20 (d, 3 H, J_{H-P} = 0.7 Hz, Me), 2.21 (d, 3 H, J_{H-P} = 0.6 Hz, Me), 2.24, 2.66, 2.74 (s, 3, 3, 3 H, 3 Me), 5.51, 5.64 (s, 1, 2 H, 3 CH(Tp*)), 6.16 (m, 1 H, CH), 6.42 (m, 2 H, CH), 8.01 (m, 1 H, CH); ^{13}C{^{1}H} NMR (C_6D_6) δ 12.4, 12.8, 12.9, 14.8, 15.2, 15.4 (s, 6 Me), 17.5 (d, $^1J_{C-P}$ = 34 Hz, PMe_3), 107.7 (s, CH(Tp*)), 107.8 (d, $^3J_{C-P}$ = 6 Hz, CH(Tp*)), 107.9 (s, CH(Tp*)), 121.1, 125.3, 126.4 (s, 3 CH), 143.2 (dd, $^1J_{C-Rh}$ or $^2J_{C-P}$ = 16 or 27 Hz, CH), 141.7, 143.5, 149.0, 151.6, 152.3 (s, 1:2:1:1:1 ratio, 6 C_q); ^{31}P{^{1}H} NMR (C_6D_6) δ 0.1 (d, $^1J_{P-Rh}$ = 132 Hz).

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