C−H Activation Reactions on Rh(I)−Ethylene Complexes of the Hydrotris(3,5-dimethylpyrazolyl)borate Ligand, Tp^{Me_2}

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N-donor Lewis bases such as acetonitrile or pyridine react with the Rh(I) compound $Tp^{Me_2}Rh(C_2H_4)_2$ (**1**) to give the Rh(III) derivatives $Tp^{Me_2}Rh(CH{=}CH_2)(C_2H_5)(L)$ (**2**, **3**) as the kinetic products of the reactions. Upon heating at 60 °C, the acetonitrile adduct **2** converts into $Tp^{Me_2}Rh(C_2H_4)(NCMe)$ (**5**). Under similar conditions, **2** is able to induce the activation of one of the C−H bonds of C_6H_6, in a process that involves the intermediacy of **1**, as demonstrated by isotopic labeling studies. The phosphine adducts $Tp^{Me_2}Rh(C_2H_4)(PR_3)$ (R = Me, Et) are also efficient reagents for the C−H bond activation of C_6H_6, py, or thiophene. In the latter case, rupture of the C−S bond is also detected, although the C−S bond activation complexes are thermodynamically disfavored with respect to those derived from the cleavage of one of the α-C−H bonds.

Introduction

In the past decades a significant number of studies have been devoted to the activation of the C−H bonds of olefinic and aromatic organic substrates by complexes of rhodium and iridium. Earlier work concentrated on M−cyclopentadienyl compounds,[1,2] for which it was often found that the formation of low-valent, electron-rich M(I) reactive unsaturated intermediates was a key step in the C−H bond cleavage reaction.

Recent work from our laboratory has focused on the study of C−H activations by Ir complexes of the hydrotris(pyrazolyl)borate ligands, Tp′.[3] A variety of substrates can be readily activated[4] in reactions that require the participation of Ir(III) species. Similar conclusions have been reached in the Cp′ system,[5] where for example the cation $Cp^*Ir(Me)(PMe_3)^+$ resulting from triflate abstraction from $Cp^*Ir(Me)(OTf)PMe_3$[5c−f] cleaves the sp^3 C−H bonds of alkanes. However, for rhodium complexes only Rh(I) intermediates appear to be implicated, in compounds both of the Cp′[1,2] and of the Tp′[6] ligands. The difference is very likely related to the relative stability of oxidation states I and III for these two elements. Whereas the Ir(I)(η-C_2H_4) formulation may be in some cases (e.g., in complexes of the Tp′ ligands) thermodynamically less favorable than the corresponding Ir(III)H($CH{=}CH_2$) isomers, for Rh, Rh(III)H($CH{=}CH_2$) compounds are thermally unstable with respect to Rh(I)(η-C_2H_4), irrespective of the nature of the auxiliary ligand (Cp′ or Tp′). The reasons for this are mostly (or exclusively) electronic and reflect the higher tendency of the 5d vs the 4d transition metals to undergo oxidation−addition reactions.[7]

As a natural extension of our studies on Tp′Ir complexes, we have investigated the chemical reactivity of the analogous Rh compounds. In a recent contribution[8]

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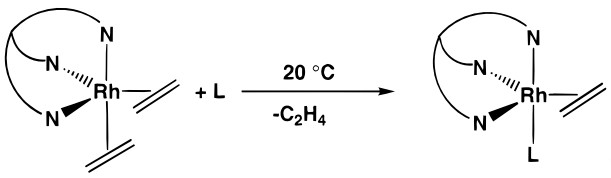
we have dealt with the reactivity of $Tp^{Me_2}Rh(C_2H_4)_2$ (**1**) and other related Rh(I) compounds toward soft donors (e.g., PR_3), H_2, and O_2. Here we describe the activation, intra- and intermolecular, of C−H bonds by some of these complexes. Part of this work has appeared in preliminary form.[9]

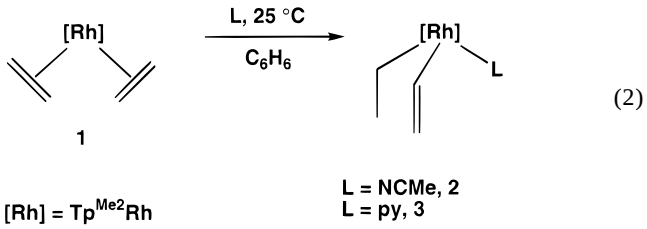
Results and Discussion

Olefinic C−H Bond Activation. We have reported recently that the room-temperature interaction of **1** with soft donors such as PR_3, CO, or CNR produces mixed Rh(I) adducts of composition $Tp^{Me_2}Rh(C_2H_4)(L)$ (eq 1),[8]



(1)

in a fast and quantitative reaction (eq 1). Contrary to this reaction outcome, the analogous interaction with the harder N-donor NCMe or NC_5H_5 (pyridine, py) yields ethylvinyl complexes of Rh(III), respectively isolated as the corresponding Lewis base adducts **2** and **3** (eq 2). These transformations are very fast and

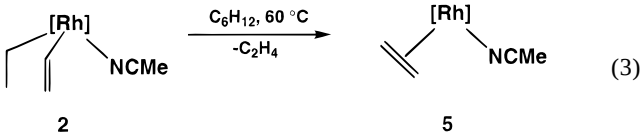


(2)

quantitative at 25 °C (NMR monitoring). On a preparative scale, compounds **2** and **3** are best obtained by dissolving **1** into the appropriate neat solvent.

The IR spectra of **2** and **3** show a medium-intensity absorption in the proximity of 2520 cm^{-1} due to ν(B−H) of the Tp^{Me_2} ligand, which is clearly in accord with the expected tridentate coordination,[10] i.e., κ^3-Tp^{Me_2}. The solution spectroscopic data are consistent with **2** and **3** having a nonsymmetric, octahedral-derived coordination geometry. Thus, the three pyrazolyl rings are inequivalent and their Me groups responsible for six resonances in their ^1H NMR spectra. $^{13}C\{^1H\}$ NMR signals at about δ 160 (see the Experimental Section) due to Rh−*C*H=CH_2 (d, ^1J(C, Rh) ≈ 25 Hz) provide further support for the proposed structure. These and other NMR signals found for **2** and **3** compare well with those reported recently by Jones and co-workers for the related chloroalkyl and chlorovinyl derivatives $Tp^{Me_2}Rh(R)Cl(CNCH_2CMe_3)$.[11a]

Solution reactivity studies effected with the acetonitrile complex **2** evince that the nitrile ligand is very labile and can be readily sustituted by $NCCD_3$ (25 °C, $t_{1/2}$ ≈ 30 min, neat CD_3CN) to give **2**-d_3, or by PMe_3 (20 °C) to form the expected adduct $Tp^{Me_2}Rh(C_2H_5)(CH=CH_2)(PMe_3)$ (**4**). In marked contrast with the chemical behavior found for the analogous iridium complex $Tp^{Me_2}Ir(C_2H_5)(CH=CH_2)(NCMe)$,[4a] the rhodium(III) derivative **2** affords the mixed Rh(I) adduct $Tp^{Me_2}Rh(C_2H_4)(NCMe)$ (**5**) when its cyclohexane solutions are heated at 60 °C for 8 h (eq 3). Monitoring of the reaction

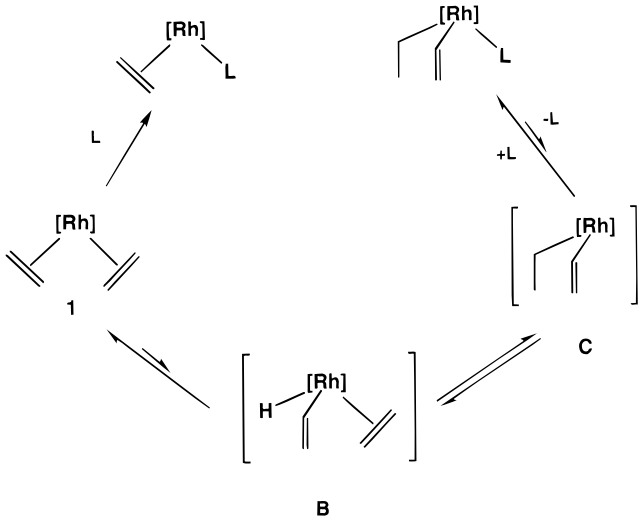


(3)

by ^1H NMR spectroscopy reveals the generation of free C_2H_4 and also of important amounts (ca. 50%) of the butadiene complex $Tp^{Me_2}Rh(\eta^4$-$C_4H_6)$ and C_2H_6. It is important to mention in this regard that the thermal decomposition (60 °C) of the bis(ethene) compound **1** gives $Tp^{Me_2}Rh(\eta^4$-$C_4H_6)$ and C_2H_6 as the major reaction products, both in the absence and in the presence of C_2H_4.[8] At the same temperature but in the presence of butadiene, the only isolated product is $Tp^{Me_2}Rh(\eta^4$-$C_4H_6)$. Carbon monoxide (20 °C) also induces the conversion of **5** into a Rh(I) product, the known bis(carbonyl) species $Tp^{Me_2}Rh(CO)_2$.[6a]

A reasonable explanation for the experimental observations just discussed is to suppose that in its interaction with Lewis bases the bis(ethene) compound **1** may follow two different reaction pathways. Soft donors such as PR_3, CO, or isocyanides prefer the Rh(I) route and give rise directly to the thermodynamic products, i.e., the Rh(I) adducts $Tp^{Me_2}Rh(C_2H_4)(L)$. Conceivably, this takes place through an associative mechanism that implies prior $\kappa^3 \rightarrow k^2$ rearrangement of the Tp^{Me_2} ligand.[8] This Rh(I) route seems to be kinetically disfavored at room temperature for the N-donors, which consequently follow the alternative Rh(III) pathway until completion of the corresponding reactions. In this route, undetectable, albeit kinetically accessible, amounts of the Rh(III) hydridovinyl isomer may be in equilibrium with the Rh(I) bis(ethene) compound **1** (Scheme 1) and experience facile olefin migratory insertion into the Rh−H bond to afford the ethylvinyl intermediate **C**. Probably, **C** is

Scheme 1



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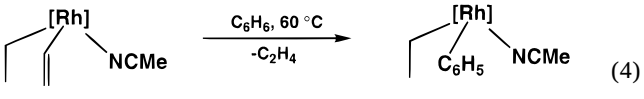
stabilized by an agostic ethyl interaction,[12] but in any event it is trapped by the Lewis base to produce the Rh(III) ethylvinyl adducts **2**−**4**. The coordinated PMe_3 ligand of **4** does not appear to be particularly labile. In contrast, the aforementioned transformation of **2** into **2**-$NCCD_3$ or **4**, by reaction with $NCCD_3$ or PMe_3, respectively, proves the facility with which its coordinated molecule of NCMe can be replaced by other donors. Hence, intermediates **C** and **B** are also accessible from the Rh(III) acetonitrile adduct **2**, and at 60 °C this system becomes under thermodynamic control and enters the Rh(I) mechanistic pathway that leads to $Tp^{Me_2}Rh(C_2H_4)$(NCMe) (**5**). Since $Tp^{Me_2}Rh(C_2H_5)$-$(CH{=}CH_2)$(NCMe) (**2**) reacts at room temperature with PMe_3 to afford $Tp^{Me_2}Rh(C_2H_5)(CH{=}CH_2)(PMe_3)$ (**4**) and $Tp^{Me_2}Rh(C_2H_4)_2$ converts into $Tp^{Me_2}Rh(C_2H_4)(PMe_3)$[8] under similar conditions, it is clear that the trapping of **C** by PMe_3 is faster than the rate of formation of **1** by means of the equilibrium involving **C**, **B**, and **1** in Scheme 1. The opposite holds for CO since it gives the Rh(I) products regardless of the reacting substrate. It should also be mentioned in this context that other data available[4a] suggest that CO would be a rather poor trapping agent for a Rh(III) species of type **C**, although once formed, the Tp^{Me_2}Rh(III)−CO bonds are particularly stable (see below). In the absence of any added Lewis base, intermediate **1** formed at the expense of **2** partially suffers its own decomposition[8] and partially reacts with the small amounts of free acetonitrile present in solution at 60 °C, to give **5**.

Clearly, and despite the fact that it is not thermodynamically favored, the easy formation of **B** and of intermediate **C** opens a thermal pathway unaccessible to the related $Cp'Rh(C_2H_4)_2$ species, which only effect vinylic activation by photolysis.[13,14]

Activation of Aromatic C−H Bonds of Organic Substrates. Unsaturated Tp^{Me_2}Ir(III) species that contain two hydrocarbyl or related monoanionic ligands are useful precursors for the activation of the C−H bonds of various organic molecules.[4b,c] For example, a Tp^{Me_2}-$Ir(C_2H_5)(CH{=}CH_2)$ fragment has proved to be a key intermediate in the scission of the C−H bonds of benzene and cyclic ethers.[4b] The knowledge of this system advises employing the Rh(III) compound Tp^{Me_2}-$Rh(C_2H_5)(CH{=}CH_2)$(NCMe), which, as discussed earlier, contains a labile NCMe ligand, for the induction of intermolecular C−H bond cleavage reactions. In accord with these expectations, upon heating a solution of **2** in benzene at 60 °C for 8 h, a smooth reaction ensues that gives the ethylphenyl derivative **6** in quantitative yield (NMR monitoring) (eq 4).

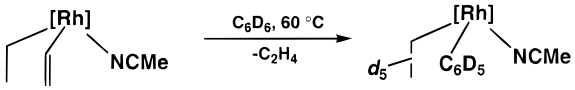


2 **6** (4)

At variance with the iridium system analogue, incorporation of a second molecule of benzene to generate a bis(phenyl) species is not observed.[4b] This dissimilarity may be a reflection of the differences in C−H bond activation mechanistic pathways as discussed below, and this divergence may rely on the thermodynamic stabilities of oxidation states I and III for Rh and Ir. As mentioned earlier in this paper, for the former element the monovalent state is relatively favored.[7]

As found for other Tp^{Me_2}M systems of this kind (M = Rh, Ir), rotation around the Rh−C_6H_5 bond is slow at 25 °C on the NMR time scale.[4b,5i,6b,e] Notwithstanding this observation, a $^{13}C\{^1H\}$ doublet at δ 159.0 (^1J(C, Rh) = 30 Hz) can confidentially be assigned to the rhodium-bound carbon atom of the aryl ligand. Other data for **6** are collected in the Experimental Section and need no further comment.

The starting and final products of the reaction of eq 4, that is, complexes **2** and **6**, respectively, differ only in the nature of one of the hydrocarbyl ligands, vinyl for the former, phenyl in the case of the latter. This structural similarity, along with the observation that the addition of NCMe considerably retards the reaction, may point to a mechanism involving the Rh(III) intermediate **C** of Scheme 1 in the crucial step of the C−H bond activation, in other words, a reaction pathway of the type proposed for the related Tp^{Me_2}Ir(III) system. Nonetheless, the experimental evidence gathered points toward a different reaction mechanism. Thus, the use of C_6D_6 gives **6**-d_{10}, that is, a product that contains perdeuterated phenyl and ethyl fragments, and GC−MS analysis of the gas evolved indicates that the ethylene produced possesses the natural isotopic distribution (eq 5). In accord with the facility with which



2 **6-d_{10}** (5)

this Tp^{Me_2}Rh(III) system reverts to Tp^{Me_2}Rh(I), we propose that the key activation step occurs in the η^2-benzene species[1a,15] **D**, as depicted in Scheme 2. Species **D** results from the substitution of one of the molecules of C_2H_4 of **1** by C_6H_6 and undergoes formal oxidative addition of an aromatic C−H bond, followed by C_2H_4 migratory insertion to produce the ethylphenyl intermediate **E** (analogous to **C** of Scheme 1). Under the conditions of the reaction this species is readily trapped by acetonitrile to afford the product, **6**. We moreover suggest that the C_2H_4-by-C_6H_6 exchange is associative and resembles in this sense the reaction of Tp^{Me_2}Rh-$(CNCH_2CMe_3)_2$ with C_6H_6, thoroughly investigated by Jones and Hessell.[6e]

An important, supplementary piece of information pertaining to these mechanistic considerations is the generation of $Tp^{Me_2}Rh(\eta^4\text{-}C_4H_6)$[8] as the major reaction product (two minor species already reported in ref 8 are also produced) when both the Rh(I) compound **1** and the Rh(III) **6** are reacted with a large excess of C_2H_4 in cyclohexane at 60 °C (Scheme 3). Evidently, this sup-

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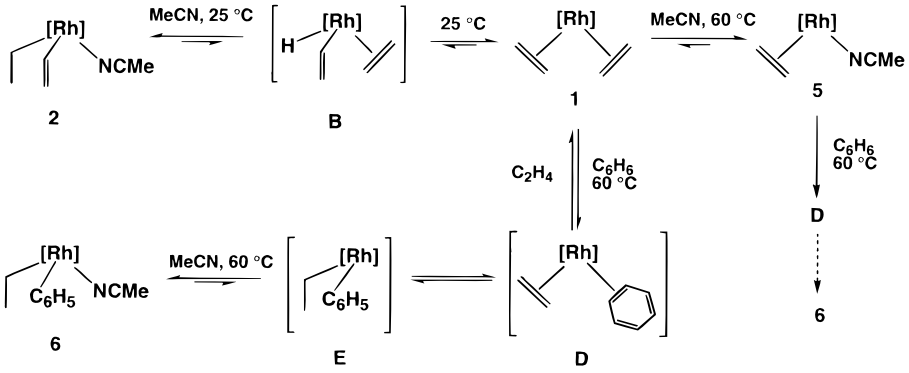
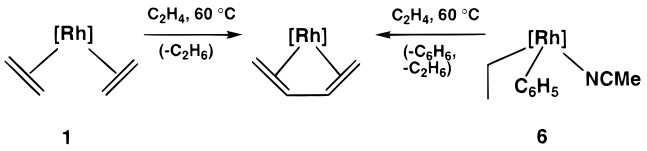
(14) Hydride−vinyl species can be active species in the evolution of other M−ethylene complexes. See for example: (a) Desrosiers, P. J.; Cai, L.; Halpern, J. *J. Am. Chem. Soc.* **1989**, *111*, 8513. (b) Burger, P.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 10462.

(15) Chin, R. M.; Dong, L.; Duckett, S. B.; Partridge, M. G.; Jones, W. D.; Perutz, R. N. *J. Am. Chem. Soc.* **1993**, *115*, 7685.

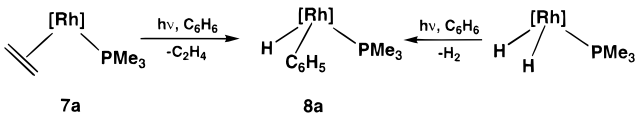
Scheme 2



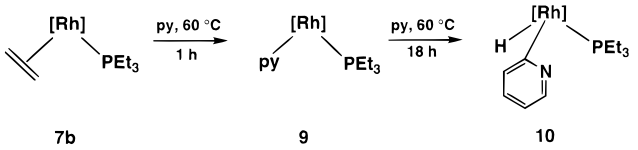
Scheme 3



Scheme 4



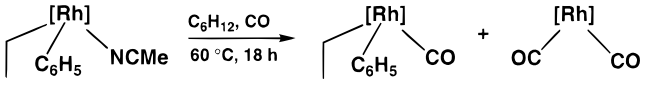
Scheme 5



ports the proposed reversibility of the C_6H_6 coordination and activation elemental steps. The mechanism of Scheme 2 provides a plausible explanation for the formation of **6**-d_{10} in C_6D_6. It seems that under the reaction conditions (i.e., in the absence of added C_2H_4) the η^2-benzene adduct **D** interchanges easily with the deuterated solvent, but the back-transformation of **D** into **1** does not take place to a measurable extent. This explains additionally the detection of ethylene with only the natural isotopic composition when C_6D_6 is used. Our experimental evidence evinces too that the mixed adduct $Tp^{Me_2}Rh(C_2H_4)(NCMe)$ (**5**) plays no intermediary role in the activation of C_6H_6 by **2**. Isolated samples of **5** convert into **6**, probably through **D**, when heated in C_6H_6, but the rate of this conversion is measurably lower than that of **2** (Scheme 1).

The acetonitrile ligand of **6** is less labile than that of **2** and does not undergo exchange with $NCCD_3$ at 25 °C during a period of 3 h. However, in accordance with the above comments and in particular with the formation of $Tp^{Me_2}Rh(\eta^4\text{-}C_4H_6)$ when **6** is reacted with C_2H_4, the deuterioacetonitrile adduct **6**−$NCCD_3$ is cleanly obtained upon heating **6** at 60 °C for 4 h in a 4:1 mixture of $C_6D_6/NCCD_3$. Note that in this case the presence of a large excess of $NCCD_3$ inhibits C_6D_6 coordination and activation by effective trapping of intermediate **E**; hence, the ethyl and phenyl ligands have normal isotopic composition.

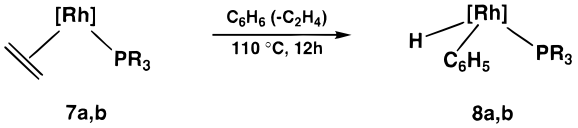
Somewhat unexpectedly, **6** reacts with CO at 60 °C (C_6H_{12}, 18 h) to give the known $Tp^{Me_2}Rh(CH_2CH_3)(C_6H_5)(CO)$,[6b] along with a small amount of $Tp^{Me_2}Rh(CO)_2$ (eq 6). This is to be compared with the reaction



(6)

of the ethylvinyl precursor **2** with CO, where only the dicarbonyl derivative is detected. On the seemingly reasonable assumption that both $Tp^{Me_2}Rh(R)(C_2H_5)$ fragments (R = Ph, $CH{=}CH_2$) have similar affinity for CO, the contrasting behavior of these two systems might rely on a smaller relative concentration of **D** in the **E** ⇌ **D** equilibrium, as compared with the **C** ⇌ **1** that, as already discussed, lies well to the right.

The recently described $Tp^{Me_2}Rh(C_2H_4)(PR_3)$ adducts[8] (PR_3 = PMe_3, **7a**; PEt_3, **7b**) are also able to effect the rupture of the C−H bonds of benzene, although more forcing conditions are needed. Heating benzene solutions of these compounds at 110 °C for about 12 h yields the hydridophenyl complexes $Tp^{Me_2}RhH(C_6H_5)(PR_3)$ (**8a,b**) in almost quantitative yield (eq 7). On the basis



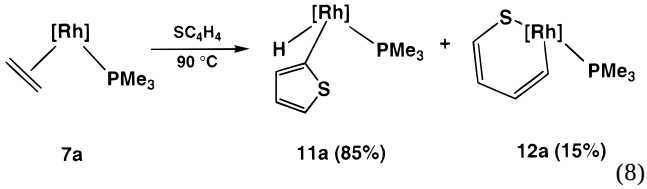
(7)

of the inertness exhibited by cyclohexane solutions of **7a** and **7b** under the same conditions and on the work of Jones et al.,[6e] we suggest that the activation of C_6H_6 occurs also through an associative process, but in contrast to the reaction described for the acetonitrile adduct **5**, the entering C_6H_6 molecule displaces the ethylene ligand. Two photochemical routes have been additionally developed for the PMe_3 derivative **8a** (Scheme 4), namely, UV irradiation of **7a** and of the recently described dihydride $Tp^{Me_2}Rh(H)_2(PMe_3)$.[8] It is probable that both involve an electron-rich Rh(I) intermediate, $Tp^{Me_2}Rh(PMe_3)$, generated by photochemical extrusion of C_2H_4 and H_2 from the respective starting products.[1,2]

Other aromatic substrates react readily with the PR_3 adducts. Thus, a stepwise reaction is observed (Scheme 5) when **7b** is heated at 60 °C in pyridine. Under these conditions the Rh(I) adduct **9** is initially generated and

then transformed into the hydride species **10** by means of a C−H bond activation that involves one of the *ortho* C−H units of the coordinated molecule of pyridine.

The thermal reaction of **7a** with thiophene is more complex and gives a mixture of two Rh(III) products in a ca. 85:15 ratio (eq 8; no intermediates are detected in



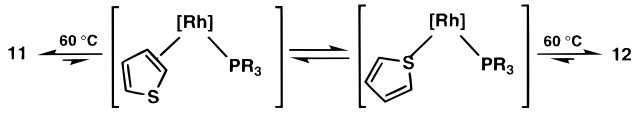
7a 11a (85%) 12a (15%) (8)

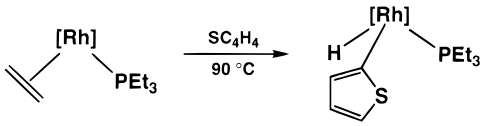
this reaction). The major product **11a** can be separated from this mixture by fractional crystallization and presents IR and ^{1}H NMR features indicative of a hydride ligand (ν(Rh−H) 2072 cm^{-1}; δ −16.55, dd, ^1J(H, Rh) = 23 Hz, ^2J(H,P) = 31 Hz). Other data collected in the Experimental Section demonstrate that it derives from the activation of one of the α-C−H bonds of thiophene.[4c,16,17] Similarly to the analogous iridium compounds,[4c] rotation around the Rh−C bond to the 2-thienyl ligand is restricted at room temperature, and the presence of rotamers is manifested by the broadening of the proton resonances associated with the Tp^{Me_2}, PMe_3, and 2-C_4H_3S groups. These signals grow to be sharper at 60 °C.

The minor complex of this reaction, **12a**, becomes the major product if the activation of thiophene is achieved by photochemical means. Irradiation of a solution of **7a** in neat thiophene yields a ca. 3:1 mixture of **12a**/**11a**, together with somewhat smaller amounts (<20% of the total) of an unidentified species. Fractional crystallization from ether/petroleum ether mixtures allows the isolation of **12a** in analytically pure form. No spectroscopic evidence indicative of a Rh−H functionality can be found in this case; instead well-defined ^{1}H multiplets corresponding to a thiophene-derived fragment are observed at δ 8.01 (1 H), 6.42 (2 H), and 6.16 (1 H). They have associated ^{13}C{^{1}H} methyne signals at δ 121.1, 125.3, 126.4, and 143.2, the latter split by coupling to the ^{103}Rh and the ^{31}P nuclei (27 and 16 Hz, respectively). These data strongly support formulation of the complex as the C−S insertion product[16] and argue in favor of the localized metallacyclic structure depicted in eq 8.

Interestingly, while the photolysis of thiophene solutions of the PEt_3 derivative **7b** under comparable conditions gives a ca. 1:1 mixture of the respective C−H and C−S activation products, **11b** and **12b** (once more accompanied by ca. 20% of an unidentified species), the thermal activation of **7b** produces **11b** almost exclusively (eq 9). Heating at 90 °C is again needed, but the reaction proceeds with more than 95% conversion into **11b**.

Scheme 6





7b 11b (9)

The C−S activation products **12** or the photolysis mixtures of **11** plus **12** remain practically unaltered in solution upon standing at room temperature. At higher temperatures (≥60 °C) in neat thiophene, they become under thermodynamic control, and a ca. 5.6:1 mixture of **11a**/**12a** and a solution containing almost exclusively **11b** are obtained for the PMe_3 and PEt_3 systems, respectively. As shown in Scheme 6 in a simplified manner, a reasonable hypothesis for the scission of the C−H and C−S bonds of thiophene assumes the formation of a Rh(I)−thiophene adduct, "Tp^{Me_2}Rh(C_4H_4S)(PR_3)", which may exist as an equilibrium mixture of the η^2-olefinic and η^1-S-bonded species.[16,17] These may respectively be proposed as the precursors of the C−H and C−S activation products, although we have been unable to gather additional information concerning the relative facility with which these processes occur.

A relevant feature of these C−X bond (X = H, S) activation reactions which merits comment at this stage is the unexpected thermodynamic preference observed for **11** vs **12**, i.e., the C−H vs the C−S scission products. This is unusual in comparison with data available on the activation of thiophenes by other transition metal compounds, where the product resulting from the cleavage of the C−S bond appears to be preferred.[4c,16,17] As a matter of fact, 2-thienyl systems seem to constitute an opening entry to the C−S insertion products. In a number of reactions of this type only the C−S bond activation products are observed,[17f,g] and in other instances irreversible rearrangement of 2-thienyls into the isomeric metallacyclic products has been demonstrated.[17d,h−j] In our case this effect may be largely steric in origin and associated with the very important spatial demands of the bulky Tp^{Me_2} ligand.

Conclusions

The formation of the Rh(III) complexes Tp^{Me_2}Rh(CH=CH_2)(C_2H_5)(L) in the reaction of Tp^{Me_2}Rh(C_2H_4)$_2$ (**1**) with N-donors such as acetonitrile or pyridine is best accounted for by assuming that under ambient conditions **1** undergoes a fast equilibrium with undetectable amounts of its hydridovinyl isomer and the unsaturated ethylvinyl intermediate "Tp^{Me_2}Rh(CH=CH_2)(C_2H_5)". Even though Rh(I) adducts such as Tp^{Me_2}Rh(C_2H_4)(NCMe) are thermodynamically favored, this reactivity contrasts with that encountered toward the soft donor CO, CNR, or PR_3, where only Rh(I) adducts were observed.[8] Deuteration studies carried out during the activation

(16) (a) Angelici, R. A. *Polyhedron* **1997**, *16*, 3073. (b) Sánchez-Delgado, R. A. *J. Mol. Catal.* **1994**, *86*, 287.

(17) See for example: (a) Selnau, H. E.; Merola, J. S. *Organometallics* **1993**, *12*, 1583. (b) Partridge, M. G.; Field, L. D.; Messerle, B. A. *Organometallics* **1996**, *15*, 872. (c) White, C. J.; Angelici, R. J. *Organometallics* **1994**, *13*, 5132. (d) Dong, L.; Duckett, S. B.; Ohman, K. F.; Jones, W. D. *J. Am. Chem. Soc.* **1992**, *114*, 151. (e) Bianchini, C.; Casares, J. A.; Osman, R.; Pattison, D. I.; Peruzzini, M.; Perutz, R. N.; Zanobini, F. *Organometallics* **1997**, *16*, 4611. (f) Ogilvy, A. E.; Draganjac, M.; Rauchfuss, T. B.; Wilson, S. R. *Organometallics* **1988**, *7*, 1171. (g) Jones, W. D.; Chin, R. M. *J. Organomet. Chem.* **1994**, *472*, 311. (h) Chisholm, M. H.; Haubrich, S. T.; Martin, J. D.; Streib, W. D. *J. Chem. Soc., Chem. Commun.* **1994**, 683. (i) Myers, A. W.; Jones, W. D.; McClements, S. M. *J. Am. Chem. Soc.* **1995**, *117*, 11740. (j) Bianchini, C.; Jiménez, M. V.; Meli, A.; Moneti, S.; Vizza, F. *J. Organomet. Chem.* **1995**, *504*, 27.

of benzene by the Rh(III) complex $Tp^{Me_2}Rh(CH{=}CH_2)(C_2H_5)(NCMe)$ demonstrate that, at variance with the Ir system analogue, Rh(I) species are key reaction intermediates. Interestingly, $Tp^{Me_2}Rh(C_2H_4)(PR_3)$ compounds react with thiophene to give both the C−H and the C−S bond activation products, with the former being thermodynamically more stable than the latter.

Experimental Section

General Comments. All preparations and manipulations were carried out under oxygen-free nitrogen following conventional Schlenk techniques. Solvents were rigorously dried and degassed before use. The complexes $Tp^{Me_2}Rh(C_2H_4)_2$ and $Tp^{Me_2}Rh(C_2H_4)(PR_3)$ were prepared according to literature procedures.[8,9a] Microanalyses were performed by the Microanalytical Service of the University of Sevilla. Many of the compounds have been subjected several times to microanalysis, and only the closest results to the calculated figures are reported here. In all the cases the C experimental figures are lower than the expected from a normal error deviation. The same behavior has been noticed by Flood et al.[11b] in some organometallic compounds of Rh and attributed to the formation of Rh−carbides or −nitrides. Infrared spectra were recorded on Perkin-Elmer models 683 and 883 and Bruker model Vector 22 spectrometers, and NMR spectra on Bruker AMX-300, DRX-400, and AMX-500 spectrometers. The ^1H and $^{13}C\{^1H\}$ resonances of the solvent were used as the internal standard, but chemical shifts are reported with respect to TMS. ^{31}P NMR shifts are referenced to external 85% H_3PO_4. Most of the NMR assignments are based on extensive $^1H-^1H$ and $^1H-^{31}P$ decoupling experiments, NOEDIFF measurements, and homo- and heteronuclear two-dimensional spectra. All spectra were obtained at 25 °C unless otherwise indicated.

$Tp^{Me_2}Rh(CH{=}CH_2)(Et)(NCMe)$ (2). Upon dissolving complex **1** (0.6 g, 1.3 mmol) in acetonitrile (20 mL), an off-white solution was rapidly formed. After the solution had been stirred for 15 min, it was concentrated at reduced pressure until cloudy and cooled overnight at −20 °C. Complex **2** was obtained as white crystals in 75% yield. ^1H NMR (C_6D_6): δ 8.36, 6.02, 5.40 (m, 1 H each, $CH_A{=}CH_MH_X$, J(A,X) = 17, J(A,M) = 9, J(M,X) = 2, J(A,Rh) = 3, J(X,Rh) = 1, J(M,Rh) = 2 Hz), 5.83, 5.76, 5.61 (s, 1 H each, 3 CH_{pz}), 2.80, 2.70 (m, 1 H each, CH_2CH_3), 2.55, 2.43, 2.39, 2.27, 2.26, 2.16 (s, 3 H each, 6 Me_{pz}), 1.09 (t, 3 H, CH_2CH_3, ^3J(H,H) = 7.5 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 158.8 (d, $RhCH{=}CH_2$, ^1J(C,Rh) = 30 Hz), 151.8, 149.1, 149.0, 143.3, 142.6, 142.2 (C_{qpz}), 118.2 (d, NCMe, ^2J(C,Rh) = 12 Hz), 117.7 ($RhCH{=}CH_2$), 107.5, 106.0, 105.7 (CH_{pz}), 16.8, 14.1, 13.7, 13.1, 13.0, 12.3, 12.1 (Me_{pz} and $RhCH_2CH_3$), 10.0 (d, $RhCH_2CH_3$, ^1J(C,Rh) = 25 Hz), −0.4 (NC*Me*); IR (Nujol): 2520 (BH), 2250 (NC) cm^{-1}. Anal. Calcd for $C_{25}H_{39}BN_9Rh$ (**2**·2NCMe): C, 51.8; H, 6.8; N, 21.8. Found: C, 51.8; H, 6.9; N, 21.7.

$Tp^{Me_2}Rh(CH{=}CH_2)(Et)(py)$ (3). Pyridine (5 mL) was added to a solid sample of compound **1** (0.20 g, 0.44 mmol), and the mixture was stirred for 30 min, during which time a pale yellow solution was formed. The solvent was then evaporated under vacuo, and a ^1H NMR spectrum of the solid, dissolved in C_6D_6, revealed quantitative formation of the title compound. It was redissolved in a mixture of CH_2Cl_2/Et_2O (1:1), and the solution obtained was concentrated in vacuo and cooled overnight to −20 °C to yield white crystals which were separated by filtration (0.09 g, 0.16 mmol, 38%). ^1H NMR (C_6D_6): δ 8.48, 6.63, 6.42, 5.86 (br, t, br, br, 1:1:1:2 ratio, NC_5H_5, ^3J(H,H) = 7.3 Hz), 8.05, 5.91, 5.33 ($CH_A{=}CH_MH_X$, J(A,X) = 16.6, J(A,M) = 9.6, J(A,Rh) = 2.2 Hz), 5.77, 5.70 (s, 2:1 ratio, 3 CH_{pz}), 2.73, 2.26 (m, 1 H each, CH_2CH_3), 2.67, 2.33, 2.32, 2.21, 1.56, 1.54 (s, 3 H each, 6 Me_{pz}), 1.04 (t, 3 H, CH_2CH_3, ^3J(H,H) = 7.4 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 161.1 (d, $RhCH{=}CH_2$, ^1J(C,Rh) = 33 Hz), 155.1, 152.2, 134.6, 123.7, 122.2 (br, br, s, br, br, NC_5H_5), 152.2, 148.9, 148.8, 143.1, 142.9, 142.4 (C_{qpz}), 119.6 ($RhCH{=}CH_2$), 107.7, 106.4, 106.3 (CH_{pz}), 17.1, 15.4, 13.7, 13.2, 12.4, 12.3, 12.2 (Me_{pz} and $RhCH_2CH_3$), 14.7 (d, $RhCH_2CH_3$, ^1J(C,Rh) = 27 Hz). IR (Nujol): 2521 cm^{-1} (BH). Anal. Calcd for $C_{24}H_{35}BN_7Rh$: C, 53.8; H, 6.5; N, 18.3. Found: C, 53.0; H, 6.4; N, 18.4.

$Tp^{Me_2}Rh(CH{=}CH_2)(Et)(PMe_3)$ (4). To a solution of complex **2** (0.17 g, 0.34 mmol) in C_6H_6 (3 mL) was added an excess of PMe_3 (0.1 mL, ca. 1 mmol), and the mixture was stirred for 5 h at room temperature. The volatiles were removed in vacuo, and the solid obtained (compound **4** >95% pure by NMR) was crystallized from a mixture of Et_2O/petroleum ether at −20 °C, to yield white crystals in 60% yield. ^1H NMR (C_6D_6): δ 8.04, 5.91, 5.12 ($CH_A{=}CH_MH_X$, J(A,X) = 17.4, J(A,M) = 9.4, J(M,X) = 2.0, J(A,Rh) = J(A,P) = 2.8, J(M,Rh) = J(M,P) = 2.0, J(X,Rh) = 2.0 Hz), 5.77, 5.71, 5.64 (s, 1 H each, 3 CH_{pz}), 2.57, 2.27, 2.26, 2.25, 2.12, (s, 1:1:2:1:1 ratio, 6 Me_{pz}), 1.02 (d, 9 H, PMe_3, ^2J(H,P) = 9.0 Hz), 0.96 (t, 3 H, CH_2CH_3, ^3J(H,H) = 7.7 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 158.0 (dd, $RhCH{=}CH_2$, ^1J(C,Rh) = 32 Hz, ^2J(C,P) = 15 Hz), 150.4, 149.6, 149.2, 143.5, 143.2, 142.4 (C_{qpz}), 119.8 (d, $RhCH{=}CH_2$, ^3J(C,P) = 5 Hz), 107.2, 107.0, 106.9 (CH_{pz}), 17.2, 16.1, 15.4, 14.8, 12.9, 12.9 (1:1:1:1:2 ratio, Me_{pz} and $RhCH_2CH_3$), 16.4 (d, PMe_3, ^1J(C,P) = 31 Hz), 8.4 (dd, $RhCH_2CH_3$, ^1J(C,Rh) = 26, ^2J(C,P) = 9 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 1.4 (d, ^1J(P,Rh) = 160 Hz). IR (Nujol): 2529 cm^{-1} (BH). Anal. Calcd for $C_{22}H_{39}BN_6PRh$: C, 49.6; H, 7.3; N, 15.8. Found: C, 48.8; H, 7.2; N, 15.6.

$Tp^{Me_2}Rh(C_2H_4)(NCMe)$ (5). Complex **2** was disolved in C_6H_{12} and the stirred solution heated (sealed ampule) at 60 °C for 8 h or at 80 °C for 1 h. After evaporation of the volatiles, the NMR analysis of the residue indicated the presence of complexes $Tp^{Me_2}Rh(\eta^4\text{-}C_4H_6)$ and **5** in a roughly 1:1 ratio. Fractional crystallization from petroleum ether could only afford a sample of complex **5** of 90% purity. ^1H NMR (C_6D_6): δ 5.94, 5.19 (s, 2:1 ratio, 3 CH_{pz}), 3.67, 2.51 (br d, 2 H each, C_2H_4, J(H,H)$_{app}$ = 10 Hz), 2.59, 2.38, 2.14, 2.13 (s, 2:2:1:1 ratio, 6 Me_{pz}), 0.33 (s, 3 H, NCMe). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 153.2, 149.5, 143.8, 142.9 (1:2:1:2 ratio, C_{qpz}), 108.7, 105.2 (1:2 ratio, CH_{pz}), 17.6 (d, C_2H_4, ^1J(C,Rh) = 17 Hz), 14.4, 13.9, 12.6, 12.3 (2:1:1:2 ratio, Me_{pz}), 3.6 (NC*Me*). IR (Nujol): 2518 cm^{-1} (BH).

$Tp^{Me_2}Rh(C_6H_5)(Et)(NCMe)$ (6). A solution of **2** (0.20 g, 0.41 mmol) in benzene (5 mL) was heated at 60 °C for 12 h. The solvent was then evaporated under reduced pressure and the white powder formed washed with cold Et_2O (−20 °C) and crystallized from a mixture of CH_2Cl_2/Et_2O at −20 °C to yield white microcrystals in ca. 40% yield. ^1H NMR (C_6D_6): δ 7.64, 7.42, 7.13, 7.09, 6.94 (d, t, d, d, t, 1 H each, C_6H_5, ^3J(H,H) = 7 Hz), 5.86, 5.77, 5.61 (s, 1 H each, 3 CH_{pz}), 2.96, 2.70 (m, 1 H each, CH_2CH_3), 2.44, 2.29, 2.28, 2.20, 1.86, 1.69 (s, 3 H each, 6 Me_{pz}), 1.06 (t, 3 H, CH_2CH_3, ^3J(H,H) = 7.5 Hz), 0.51 (s, 3 H, NCMe). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 159.0 (d, RhC_{ar}, ^1J(C,Rh) = 30 Hz), 152.2, 149.0, 149.0, 143.2, 142.8, 142.1 (C_{qpz}), 140.6, 137.8, 126.0, 125.5, 121.1 (CH_{ar}), 118.4 (d, NCMe), ^2J(C,Rh) = 8 Hz), 107.8, 106.0, 105.9 (3 CH_{pz}), 16.9, 14.0, 13.5, 13.2, 13.1, 12.4, 12.2 (Me_{pz} and $RhCH_2CH_3$), 11.7 (d, $RhCH_2CH_3$, ^1J(C,Rh) = 25 Hz), 0.8 (NC*Me*). IR (Nujol): 2527 cm^{-1} (BH).

$Tp^{Me_2}RhH(C_6H_5)(PMe_3)$ (8a). A solution of the complex $Tp^{Me_2}Rh(C_2H_4)(PMe_3)$ (0.11 g, 0.22 mmol) in C_6H_6 (10 mL) was heated at 110 °C for 12 h. The volatiles were removed in vacuo and the residue crystallized from petroleum ether at −20 °C. Yield: 70%. ^1H NMR (C_6D_6): δ 7.65, 7.22, 7.12, 7.00, 6.83 (d, d, t, t, t, 1 H each, C_6H_5, ^3J(H,H = 7.3 Hz), 5.87, 5.67, 5.47 (s, 1 H each, CH_{pz}), 2.38, 2.26, 2.20, 2.13, 2.05, 1.74 (s, 3 H each, 6 Me_{pz}), 1.15 (dd, 9 H, PMe_3, ^2J(H,P) = 9.2, ^3J(H,Rh) = 0.6 Hz), −16.90 (dd, 1 H, ^1J(H,Rh) = 25.1, ^2J(H,P) = 30.3 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 150.6, 149.7, 149.2, 144.0, 143.4, 142.4 (C_{qpz}), 144.4, 140.6, 125.8, 125.5, 121.1 (CH_{ar}), 106.7, 106.1, 105.9 (CH_{pz}), 19.5 (d, PMe_3, ^1J(C,P) = 32 Hz), 16.6, 16.5, 14.8, 12.8, 12.7, 12.5 (Me_{pz}). $C_{ar}Rh$ was not located. $^{31}P\{^1H\}$ NMR (C_6H_6): δ 1.64 (d, ^1J(P,Rh) = 146 Hz); IR (Nujol): 2520 (BH),

2070 (RH) cm^{-1}. Anal. Calcd for $C_{26}H_{37}BN_6PRh$: C, 52.0; H, 6.7; N, 15.2. Found: C, 50.5; H, 6.7; N, 14.4.

$Tp^{Me_2}Rh(H)(C_6H_5)(PEt_3)$ (8b). This complex was obtained from $Tp^{Me_2}Rh(C_2H_4)(PEt_3)$ following a procedure similar to that describe above for **8a**. Yield: 50%. ^1H NMR (C_6D_6): δ 7.84, 7.26, 7.12, 6.99, 6.82 (d, d, td, td, td, 1 H each, C_6H_5, $^3J(H,H) \approx 7.5$, $J(H,H) \approx 1$ Hz), 5.88, 5.64, 5.44 (s, 1 H each, 3 CH_{pz}), 2.43, 2.30, 2.22, 2.14, 2.10, 1.73 (s, 3 H each, 6 Me_{pz}), 1.60 (m, 6 H, 3 PCH_2CH_3), 0.70 (m, 9 H, 3 PCH_2CH_3), −16.50 (dd, 1 H, $^1J(H,Rh) \approx {}^2J(H,P) = 25$ Hz). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 154.0 (dd, RhC_{ar}, $^1J(C,Rh) = 32$, $^2J(C,P) = 13$ Hz), 150.5, 150.1, 149.9, 144.6, 143.5, 142.5 (C_{qpz}), 146.4, 141.3, 125.6, 125.0, 121.1 (CH_{ar}), 107.0, 106.2, 105.8 (CH_{pz}), 18.8 (d, PCH_2, $^1J(C,P) = 28$ Hz), 16.2, 15.8, 14.6, 12.8, 12.7, 12.6 (Me_{pz}), 7.35 (PCH_2CH_3). $^{31}P\{^1H\}$ NMR (C_6H_6): δ 27.6 (d, $^1J(P,Rh) = 144$ Hz). IR (Nujol): 2092 cm^{-1} (RhH). IR (Nujol): 2513 cm^{-1} (BH). Anal. Calcd for $C_{27}H_{43}BN_6PRh$: C, 54.4; H, 7.3; N, 14.0. Found: C, 54.4; H, 7.4; N, 13.5.

$Tp^{Me_2}Rh(NC_5H_5)(PEt_3)$ (9). Complex $Tp^{Me_2}Rh(C_2H_4)(PEt_3)$ (0.14 g, 0.25 mmol) was dissolved in 10 mL of pyridine. The resulting solution was heated at 60 °C for 1 h. The solvent was evaporated in vacuo and the residue analyzed by NMR spectroscopy. This material was 90% pure by this analysis, but all the crystallization attempts to liberate it from impurities were fruitless. ^1H NMR (C_6D_6): δ 10.20, 8.89, 6.45, 6.30 (br, 1 H each, NC_5H_5), 6.02, 5.63, 5.62 (s, 1 H each, CH_{pz}), 2.53, 2.42, 2.33, 2.32, 2.27, 1.55 (s, 3 H each, 6 Me_{pz}), 1.10 (m, 3 H, 3 $PCHCH_3$), 0.90 (m, 3 H, 3 $PCHCH_3$), 0.80 (m, 9 H, 3 PCH_2CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 158.2, 155.8, 136.8, 122.8, 121.9 (CH_{py}), 149.8, 147.7, 146.0, 145.2, 144.3, 141.6 (C_{qpz}), 105.2, 105.1, 105.0 (CH_{pz}), 17.8 (d, PCH_2, $^1J(C,P) = 11$ Hz), 16.8, 14.2, 14.0, 13.3, 13.2, 12.6 (Me_{pz}), 7.8 (PCH_2CH_3). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 25.9 (d, $^1J(P,Rh) = 194$ Hz).

$Tp^{Me_2}RhH(C_5H_4N)(PEt_3)$ (10). Complex $Tp^{Me_2}Rh(C_2H_4)(PEt_3)$ (0.3 g, 0.55 mmol) was dissolved in pyridine (10 mL) and the resulting solution heated, with stirring, at 60 °C for 18 h. The solvent was stripped off in vacuo and the residue crystallized from petroleum ether at −20 °C. Yield: 35%. ^1H NMR (C_6D_6): δ 8.48, 7.09, 6.51, (dd, d, m, H^3, H^6, H^4−H^5, 1:1:2 ratio, C_5H_4N, $J(H^3,H^4) = 4.5$, $J(H^3,H^5) = 1.5$, $J(H^5,H^6) = 7.7$ Hz), 5.86, 5.64, 5.50 (s, 1 H each, 3 CH_{pz}), 2.53, 2.42, 2.30, 2.25, 2.14, 1.95 (s, 3 H each, 6 Me_{pz}), 0.90 (m, 15 H, 3 PCH_2CH_3), −15.8 (t, 1 H, RhH, $^1J(H,Rh) \approx {}^2J(H,P) = 25.5$ Hz). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 150.2, 150.0, 149.8, 144.3, 143.7, 142.7, (C_{qpz}), 145.8, 135.8, 129.7, 115.6 (CH_{py}), 106.8, 106.2, 105.6 (CH_{pz}), 18.8 (d, PCH_2, $^1J(C,P) = 28$ Hz), 16.2, 16.1, 14.9, 12.9, 12.7, 12.5 (Me_{pz}), 7.7 (d, PCH_2CH_3, $^2J(C,P) = 3$ Hz). $C_{ar}Rh$ was not located. $^{31}P\{^1H\}$ NMR (C_6H_6): δ 29.4 (d, $^1J(P,Rh) = 150$ Hz). IR (Nujol): 2513 (BH), 2094 (RH) cm^{-1}. Anal. Calcd for $C_{26}H_{42}BN_7PRh$: C, 52.3; H, 7.0; N, 16.4. Found: C, 51.5; H, 6.7; N, 16.5.

$Tp^{Me_2}RhH(2\text{-}C_4H_3S)(PMe_3)$ (11a). Complex $Tp^{Me_2}Rh(C_2H_4)(PMe_3)$ (0.05 g, 0.1 mmol) was dissolved in thiophene (3 mL) and heated at 90 °C for 4 h. The volatiles were removed in vacuo, and the residue was fractionally crystallized from Et_2O/petroleum ether to afford complex **11a** in ca. 30% yield. ^1H NMR (C_6D_6): δ 7.31, 6.98, 6.66 (d, dd, br d, 1 H each, C_4H_3S, $J(H,H) = 5.1$ and 3.0 Hz), 5.82, 5.61, 5.44 (s, 3 H, 3 CH_{pz}), 2.39, 2.27, 2.18, 2.16, 2.14, 1.76 (s, 3 H each, 6 Me_{pz}), 1.24 (d, 9 H, PMe_3, $^2J(H,P) = 9.5$ Hz), −16.55 (dd, 1 H, RhH, $^1J(H,Rh) = 22.6$ Hz, $^2J(H,P) = 31.1$ Hz). $^{31}P\{^1H\}$ NMR (C_6H_6): δ 1.2 (d, $J(P,Rh) = 146$ Hz). IR (Nujol): 2072 cm^{-1} (RhH).

$Tp^{Me_2}Rh(SCHCHCHCH)(PMe_3)$ (12a). A solution of complex $Tp^{Me_2}Rh(C_2H_4)(PMe_3)$ (0.23 g, 0.45 mmol) in thiophene (50 mL) was transferred to a Pyrex photoreactor refrigerated with water and irradiated (Hg lamp) for 2 h at room temperature. After the volatiles were removed, the residue was fractionally crystallized from Et_2O/petroleum ether mixtures to give an orange microcrystalline solid (40% yield). ^1H NMR (C_6D_6): δ 8.01, 6.42, 6.16 (m, 1:2:1 ratio, SC_4H_4), 5.64, 5.51 (s, 2:1 ratio, 3 CH_{pz}), 2.74, 2.66, 2.24, 2.21, 2.20, 2.10 (s, 3 H each, 6 Me_{pz}), 1.17 (d, 9 H, PMe_3, $^2J(H,P) = 9.9$ Hz). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 152.3, 151.6, 149.0, 143.5, 143.5, 141.7 (C_{qpz}), 143.2, 126.4, 125.3, 121.1 (dd, s, s, s, SC_4H_4, $^1J(C,Rh) = 30$, $^2J(C,P) = 16$ Hz), 107.9, 107.8, 107.7 (s, d, s, CH_{pz}, $J(C,P) = 6$ Hz), 17.5 (d, PMe_3, $^1J(C,P) = 34$ Hz), 15.4, 15.2, 14.8, 12.9, 12.8, 12.4 (Me_{pz}). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 0.1 (d, $^1J(P,Rh) = 132$ Hz). Anal. Calcd for $C_{22}H_{35}BN_6PSRh$: C, 47.2; H, 6.3; N, 15.0. Found: C, 47.2; H, 6.0; N, 14.8.

$Tp^{Me_2}RhH(2\text{-}C_4H_3S)(PEt_3)$ (11b). This complex was obtained in almost quantitative yield (NMR) following the procedure described above for the PMe_3 analogue. To obtain crystals of this compound, the solid obtained after evaporation of the solvent was dissolved in petroleun ether and the solution filtered, concentrated under vacuo, and cooled to −20 °C, to yield brown crystals. ^1H NMR (C_6D_6): δ 7.39, 7.06, 6.71 (br, 1 H each, C_4H_3S), 5.87, 5.61, 5.44 (s, 1 H each, 3 CH_{pz}), 2.40, 2.27, 2.27, 2.17, 2.06, 1.82 (s, 3 H each, 6 Me_{pz}), 1.68 (m, 6 H, 3 PCH_2CH_3), 0.69 (m, 9 H, 3 PCH_2CH_3), −16.10 (br t, 1 H, RhH, $^1J(H,Rh) = {}^2J(H,P) = 25$ Hz). $^{31}P\{^1H\}$ NMR (C_6H_6): δ 27.7 (d, $^1J(P,Rh) = 134$ Hz). IR (Nujol): 2519 cm^{-1} (BH). Anal. Calcd for $C_{25}H_{41}BN_6PSRh$: C, 49.8; H, 6.8; N, 13.9. Found: C, 50.3; H, 6.9; N, 14.0.

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