Control of η^2-Coordination vs C–H Bond Activation by Rhodium: The Role of Aromatic Resonance Energies

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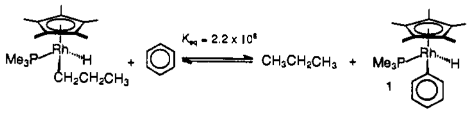
Abstract: The reactions of a series of fused polycyclic arenes with $(C_5Me_5)Rh(PMe_3)(Ph)H$ and $(C_5H_5)Rh(PMe_3)(Ph)H$ have been examined, and the thermodynamic preferences for η^2-arene coordination vs C–H bond activation have been determined. While naphthalene, perylene, and triphenylene give equilibrium mixtures of both C–H activation and η^2-complexes, phenanthrene, anthracene, 2-methoxynaphthalene, 2,6-dimethoxynaphthalene, pyrene, and fluoranthene give only η^2-complexes (C_5Me_5 complexes). Naphthalene and several of the polycyclic aromatics are found to give bis-η^2-complexes upon extended reaction. Electron-withdrawing groups as in p-$C_6H_4(CF_3)_2$ and m-$C_6H_4(CF_3)_2$ are also found to promote η^2-coordination in monocyclic arenes (C_5H_5 complexes). A C_5H_5 ligand favors η^2-coordination compared to a C_5Me_5 ligand, as does rhodium compared to iridium. The effects of resonance, specifically the differences in the Hückel energies of the η^2-bound vs free ligand, are believed to control the C–H activation/η^2-coordination equilibria in polycyclic systems. The perylene complex $(C_5Me_5)Rh(PMe_3)(\eta^2\text{-perylene})$ has been found to crystallize in monoclinic space group $C2/c$, with $a = 32.927(10)$ Å, $b = 10.125(2)$ Å, $c = 18.129(8)$ Å, $\beta = 100.30(3)°$, $V = 5946.5(6.3)$ Å^3, and $Z = 8$.

Introduction

The reactions of coordinatively unsaturated metal complexes with hydrocarbons have been the subject of intense study during the past decade.[1,2] Of the metal complexes that react with hydrocarbons by oxidative addition pathways, the $[(C_5H_5)Rh(PMe_3)]$ and $[(C_5Me_5)Rh(PMe_3)]$ systems are perhaps the most thoroughly understood.[3] In particular, the ability of aromatic hydrocarbons to coordinate in the η^2-mode prior to C–H activation has been demonstrated. Further examination of the reactions with fused, polycyclic aromatics has revealed the origin of the tendency to form η^2-complexes with arenes.

The initial studies undertaken in our laboratories were aimed at using the same metal/ligand systems, $[(C_5Me_5)Rh(PMe_3)]$ and $[(C_5H_5)Rh(PMe_3)]$, to study a series of hydrocarbon activation reactions with the goal of extracting some basic thermodynamic parameters about the addition reactions. The thermodynamics of the oxidative addition of benzene and propane to the $[(C_5Me_5)Rh(PMe_3)]$ fragment were mapped out, and it was demonstrated that η^2-complexation of the benzene precedes C–H activation. The combination of kinetic data from several reactions allowed the calculation of the free energy difference separating $(C_5Me_5)Rh(PMe_3)(Ph)H$ + propane from $(C_5Me_5)Rh(PMe_3)(n\text{-Pr})H$ + benzene, which gave an equilibrium constant of 2.2×10^6 favoring benzene activation (eq 1).[4] A similar situation is apparently the case for the C_5H_5 analog, with the phenyl hydride derivative being much more stable than the alkyl hydride complex[5] and an η^2-C_6H_6 complex being formed prior to C–H bond oxidative addition.[6]



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Evidence for the η^2-benzene complex was indirect at first, being a proposed intermediate in the intramolecular rearrangement of $(C_5Me_5)Rh(PMe_3)(p\text{-tolyl})H$ to $(C_5Me_5)Rh(PMe_3)(m\text{-tolyl})H$ or of $(C_5Me_5)Rh(PMe_3)(C_6D_5)H$ to $(C_5Me_5)Rh(PMe_3)(C_6D_4H)D$.[7] Further detailed studies of the isotope effects in both the oxidative addition and the reductive elimination reactions were also interpreted in terms of an η^2-benzene intermediate.[8] Recently, flash photolysis studies have provided direct evidence for this species prior to C–H insertion with both the C_5H_5 and C_5Me_5 derivatives.[6,9] These studies showed that the intermediate $[(C_5Me_5)Rh(PMe_3)]$ reacts rapidly (<200 ns) to give the η^2-C_6H_6 complex, which then goes on more slowly ($\tau \cong 150$ μs) to insert into the C–H bond (eq 2). The activation parameters for this step of the reaction were also determined, giving $\Delta H^\ddagger = 11.15(0.31)$ kcal/mol and $\Delta S^\ddagger = -4.9(1.1)$ eu. Studies of the $[(C_5H_5)Rh(PMe_3)]$ fragment showed it to react more slowly ($\tau \cong 700$ μs), with $\Delta H^\ddagger = 11.48(0.43)$ kcal/mol and $\Delta S^\ddagger = -6.9(1.6)$ eu.

With the C_5Me_5 system, η^2-arene complexes were readily observed under ambient conditions with C_6F_6[10] and with fused polycyclic aromatic systems.[11,12] The C_5H_5 system has shown the ability to form η^2-complexes with p-$C_6H_4(CF_3)_2$[9] and with C_6F_6.[10] The extension of these studies to larger fused polycyclic

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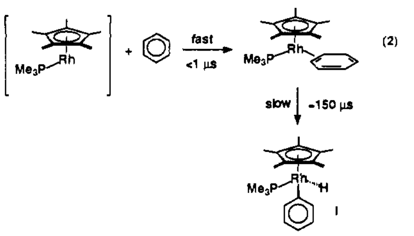
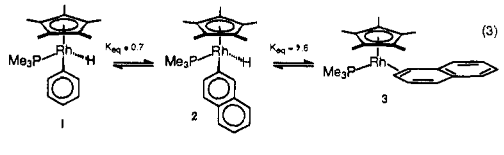


aromatic shows a continuing trend leading to the formation of new η^2-arene complexes. Details of the reactions with naphthalene, other polycyclic aromatics, and $C_6H_4(CF_3)_2$ are presented below.

Results

Reaction of [(C_5Me_5)Rh(PMe_3)] with Naphthalene and Benzene. (C_5Me_5)Rh(PMe_3)(Ph)H (**1**) when heated to 60 °C serves as an efficient thermal source of the coordinatively unsaturated fragment [(C_5Me_5)Rh(PMe_3)]. In the presence of excess naphthalene, complete conversion to a 1:2 mixture of the naphthyl hydride complex (C_5Me_5)Rh(PMe_3)(2-naphthyl)H (**2**) and the η^2-naphthalene complex (C_5Me_5)Rh(PMe_3)(η^2-$C_{10}H_8$) (**3**) was observed. The formation of the η^2-complex is readily indicated by the appearance of high-field resonances for the protons of the coordinated double bond of the arene at δ 3.213 (td, $J_{H-H} = J_{P-H} = 7.4$ Hz, $J_{Rh-H} = 2.5$ Hz, as determined by ^{1}H–^{1}H and ^{1}H–^{31}P decoupling experiments) and 3.629 (td, $J_{H-H} = J_{P-H} = 7.4$ Hz, $J_{Rh-H} = 2.5$ Hz). Furthermore, **2** and **3** were found to be in a dynamic equilibrium by ^{31}P spin saturation transfer (SST) experiments, indicating that these species interconvert once every few seconds at 25 °C. The activation parameters for the rate of loss of the naphthyl hydride complex were determined as $\Delta H^\ddagger = 16.9(7)$ kcal/mol, $\Delta S^\ddagger = -8.1(2)$ eu,[9] which compare favorably with the previously determined values for the formation of (C_5Me_5)Rh(PMe_3)(η^2-p-xylene) from (C_5Me_5)Rh(PMe_3)(p-xylyl)H ($\Delta H^\ddagger = 16.3(2)$ kcal/mol, $\Delta S^\ddagger = -6.3(8)$ eu).[3] These values indicate that the stabilization of the η^2-naphthalene complex has little effect upon the transition state for aryl hydride to η^2-arene interconversion. Thermolysis of this mixture (51 °C) in benzene-d_6 allowed the determination of the barrier for naphthalene dissociation by measuring the rate of the arene exchange ($k = 1.1 \times 10^{-5}$ s^{-1}). This rate corresponds to a free energy barrier of 26.4 kcal/mol.

In the presence of a 1:1 mixture of benzene and naphthalene, three species are formed as shown in eq 3. At 60 °C, the arenes



are labile (intermolecular arene exchange occurs), so that this distribution represents an equilibrium mixture of the compounds. The observation of comparable amounts of compounds **1**, **2**, and **3** indicates that there is little difference in the free energies of the complexes. By comparison, the η^2-benzene complex (C_5Me_5)Rh(PMe_3)(η^2-C_6H_6) is much higher in energy, by ~7 kcal/mol. The temperature dependence of the **2** ⇌ **3** equilibrium allows the determination of the enthalpy and entropy from a Van't Hoff plot (Figure 1) as $\Delta H° = -4.13(0.02)$ kcal/mol and $\Delta S° = -12.0(0.1)$ eu. The thermodynamic data for these complexes can be easily compared using the free energy picture shown in Scheme I.

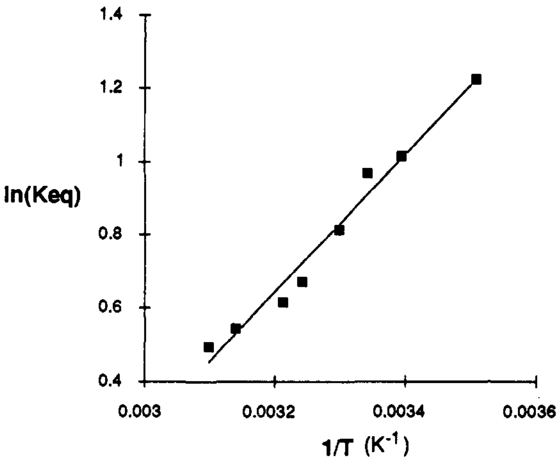
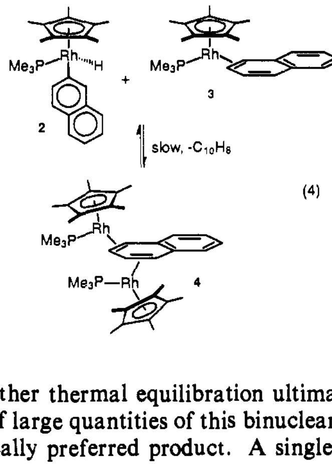


Figure 1. Van't Hoff plot for the equilibrium between (C_5Me_5)Rh(PMe_3)(naphthyl)H and (C_5Me_5)Rh(PMe_3)(η^2-naphthalene).

The kinetic product of the reaction of [(C_5Me_5)Rh(PMe_3)] with naphthalene at low temperature is the η^2-arene complex **3**. This was discovered by irradiation of (C_5Me_5)Rh(PMe_3)H_2 in methylcyclohexane-d_{14} at low temperature to generate the thermally labile complex (C_5Me_5)Rh(PMe_3)(C_7D_{13})D. Upon warming the sample to −30 °C in the presence of naphthalene, the first product observed following alkane elimination was **3**. Upon warming to 25 °C, naphthyl hydride complex **2** was seen to appear at the expense of **3**, until equilibrium was achieved.[9]

By way of comparison, the C_5H_5 complex was also examined for its tendency to form η^2-complexes with naphthalene. The lesser electron-donating capability of the C_5H_5 ligand compared with C_5Me_5 would imply a reduced tendency toward C–H oxidative addition. Indeed, the reaction of naphthalene with (C_5H_5)Rh(PMe_3)(Ph)H proceeds at 40 °C to give exclusively the η^2-naphthalene complex, with no C–H activation product being observed. The η^2-bound olefinic hydrogens appear at δ 3.49 (qd, $J = 5.6$, 2.4 Hz) and 4.09 (td, $J = 6.6$, 2.6 Hz). A ^{1}H–^{1}H COSY NMR spectrum allowed assignment of these features as the β and α resonances, respectively. The ^{31}P NMR spectrum shows a doublet at δ 3.76 ($J = 200$ Hz) characteristic of a (C_5H_5)Rh(I) species.

Continued heating of the equilibrium mixture of **2** and **3** results in the formation of a new product in which two metals are coordinated to a single aromatic ring, [(C_5Me_5)Rh(PMe_3)]$_2$(1,2-η^2-3,4-η^2-naphthalene) (**4**) (eq 4).[13] Removal of free naphthalene



followed by further thermal equilibration ultimately results in the formation of large quantities of this binuclear species as the thermodynamically preferred product. A single-crystal X-ray study of **4** confirmed that both metals are bound to opposite faces of the same ring. The molecule has a C_2 axis of rotation lying along the long axis of the naphthalene ring. The Rh1–C1–C2

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[11] The generation of [(C_5Me_5)Rh(PMe_3)] with p-di-tert-butylbenzene leads to the formation of the η^2-complex at low temperature, but the complex decomposes above 0 °C.[3]

[12] Jones, W. D.; Dong, L. *J. Am. Chem. Soc.* **1989**, *111*, 8722–8723.

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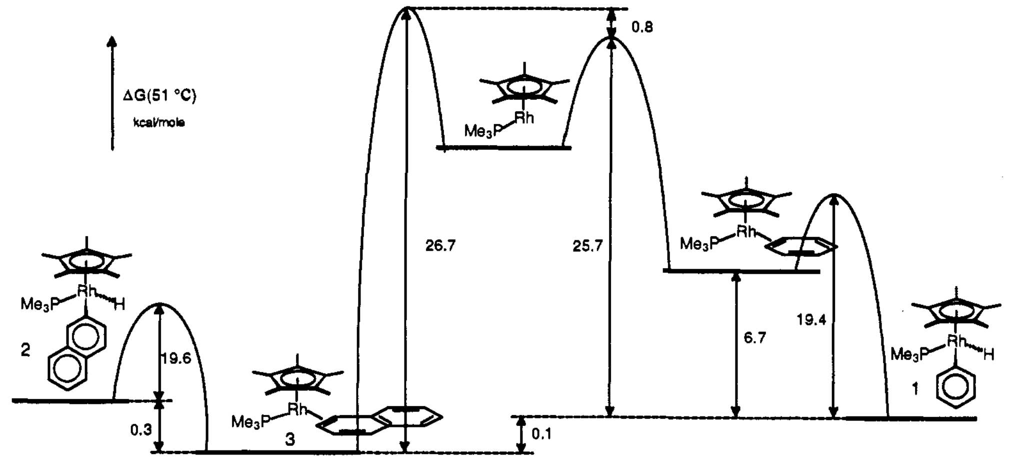
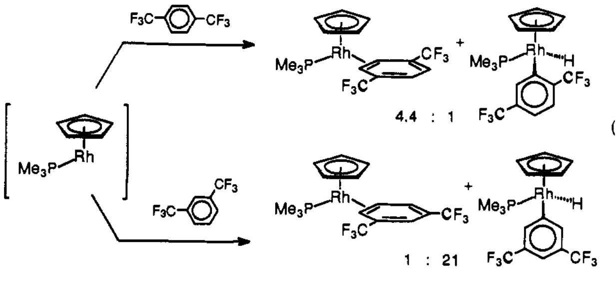
Scheme I



and Rh2–C3–C4 planes which define the η^2-coordination are tilted 113° and 114°, respectively, away from the naphthalene plane. The analogous binuclear product was also detected by NMR spectroscopy upon prolonged thermolysis of $(C_5H_5)Rh(PMe_3)(\eta^2$-naphthalene).

The reaction of phenyl hydride **1** with styrene was examined as an analogy of a π-system attached to an arene ring. Two products are formed in a 2.5:1 ratio, both of which were assigned as rotamers of the η^2-styrene adduct $(C_5Me_5)Rh(PMe_3)(\eta^2$-styrene). The ^{31}P NMR data were consistent with two Rh(I) complexes, with two doublets seen at δ –0.90 (J = 194 Hz) and –6.54 (J = 203 Hz).

The photochemical reaction of $(C_5H_5)Rh(PMe_3)(C_2H_4)$ or $(C_5H_5)Rh(PMe_3)H_2$ with 1,4-bis(trifluoromethyl)benzene leads to the formation of two products in a 4.4:1 ratio when dissolved in C_6D_6. ^{31}P NMR spectroscopy shows the major species at δ 1.25 (J = 188.3 Hz) and the minor species at 12.10 (J = 152 Hz). The ^1H NMR spectrum shows a doublet of doublets at δ 3.34 and a singlet at 6.26 (area 2 H each) for the major product and a hydride resonance at –13.23 for the minor product, in addition to C_5H_5 and PMe_3 resonances for each compound. The ^{19}F NMR spectrum shows a singlet at δ 64.82 for the major product and two smaller resonances at –58.67 and –62.38 for the minor product. These observations are consistent with the assignment of the major species as the symmetrical η^2-arene product, $(C_5H_5)Rh(PMe_3)[\eta^2\text{-}C_6H_4(CF_3)_2]$, and of the minor product as the C–H insertion adduct, $(C_5H_5)Rh(PMe_3)[2,5\text{-}C_6H_3(CF_3)_2]H$ (eq 5). In contrast, the thermal reaction of $(C_5Me_5)Rh(PMe_3)(Ph)H$ with 1,4-bis(trifluoromethyl)benzene leads to the formation of the C–H activation adduct only, with no observation of the η^2-complex. Irradiation of $(C_5H_5)Ir(PMe_3)H_2$ in the presence of 1,4-bis(trifluoromethyl)benzene also gives exclusively the C–H insertion product.



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The equilibrium between these two isomers of the C_5H_5 complex was demonstrated by observing a reproducible change in the equilibrium constant upon changing the solvent from benzene to acetonitrile and other solvents (Table I). The equilibration of the aryl hydride and η^2-arene isomers was also demonstrated qualitatively using spin saturation transfer (SST) at 333 K.[14] Inversion of the magnetization of the C_5H_5 resonance for the η^2-1,4-bis(trifluoromethyl)benzene complex resulted in a decrease in the intensity of the resonance for the aryl hydride complex. The relaxation time, T_1, of the C_5H_5 resonance for the η^2-arene complex (22.3 s) proved to be much shorter than the T_1 of the C_5H_5 resonance for the aryl hydride complex (45.5 s), and consequently only an approximate value for the rate of interconversion could be obtained (k = 0.4 s^{-1}).

Table I. Equilibrium Constants at 291 K for $(C_5H_5)Rh(PMe_3)[2,5\text{-}(CF_3)_2C_6H_3]H \rightleftharpoons (C_5H_5)Rh(PMe_3)[\eta^2\text{-}1,4\text{-}(CF_3)_2C_6H_4]$

solvent	K_{eq}	$\Delta G°$ (kcal/mol)	solvent	K_{eq}	$\Delta G°$ (kcal/mol)
benzene	4.4	–0.84	THF	3.0	–0.63
cyclohexane	4.0	–0.79	acetonitrile	2.9	–0.61
acetone	3.4	–0.70			

The photochemical reaction of $(C_5H_5)Rh(PMe_3)(C_2H_4)$ with 1,3-bis(trifluoromethyl)benzene gives two products in a 20.7:1 ratio. The major species displays a ^{31}P doublet at δ 13.83 (J = 151 Hz), a ^{19}F singlet at δ –62.31, and ^1H resonances at δ –13.65 (dd, J = 41.8, 30.5 Hz, 1 H), 8.08 (s, 2 H), and 7.56 (s, 1 H), as well as C_5H_5 and PMe_3 resonances, that allow it to be characterized as the C–H insertion product $(C_5H_5)Rh(PMe_3)[3,5\text{-}C_6H_3(CF_3)_2]H$. The minor isomer displays a ^{31}P doublet at δ 2.99 (J = 188 Hz) and a C_5H_5 ^1H resonance shifted 0.4 ppm upfield of the C–H insertion product. These features parallel the NMR data for the η^2-1,4-$C_6H_4(CF_3)_2$ complex described above. On this basis we assign the minor product as $(C_5H_5)Rh(PMe_3)[4,5\text{-}\eta^2\text{-}1,3\text{-}C_6H_4(CF_3)_2]$ (eq 5). This molecule should have four inequivalent arene protons and inequivalent CF_3 groups. The assignment is confirmed by ^1H NMR spectra recorded with very high signal-to-noise ratios which reveal three of the ^1H resonances: δ 7.63 (d, J = 8.1 Hz, 1 H), 6.73 (s, 1 H), and 3.07 (m, 1 H). The ^{19}F resonances are located at δ –63.09 and –62.20.

The reaction of the less electron rich complex $(C_5H_5)Rh[P(OMe)_3](C_2H_4)$ with 1,4-bis(trifluoromethyl)benzene was also examined. Irradiation in neat arene results in the formation of two new products. The minor product has resonances similar to those of $(C_5H_5)Rh(PMe_3)[\eta^2\text{-}C_6H_4(CF_3)_2]$ for the protons at and opposite the site of coordination, which appear at δ 4.09 (t) and 6.28 (s), respectively. The C_5H_5 and $P(OMe)_3$ resonances appear at δ 4.83 (dd) and 3.20 (d). The two equivalent CF_3 groups in the coordinated arene appear at δ –64.77 in the ^{19}F NMR spectrum. No sign of any C–H activation products was detected. The major product had a C_5H_5 resonance at δ 4.81

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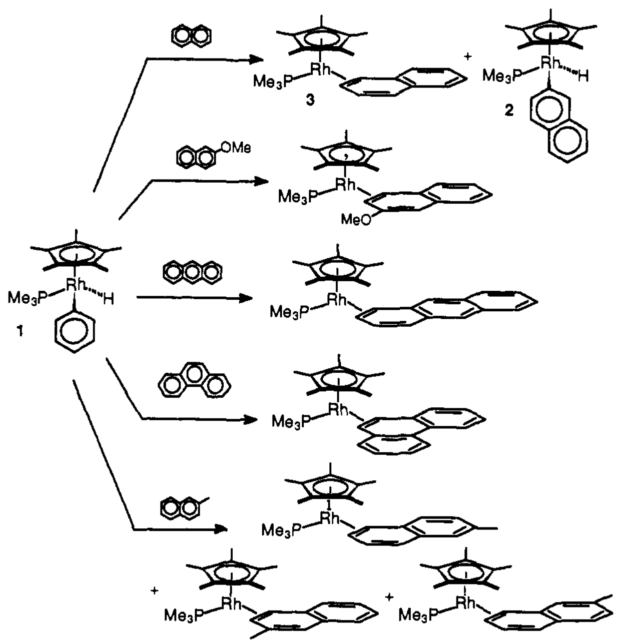
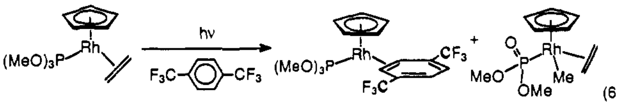
(14) Dahlquist, F. W.; Longmuir, K. J.; Du Vernet, R. B. *J. Magn. Reson.* **1975**, *17*, 406.

Scheme II



(dd), but there was no $P(OMe)_3$ resonance. There were two overlapping doublets at δ 3.65 and 3.63. A third resonance of the same area was observed as a triplet at δ 1.16. Coordinated ethylene resonances were seen at δ 3.39 and 2.77. The $^{13}C\{^1H\}$ DEPT NMR spectrum showed a resonance at δ −12.75 that was coupled to both rhodium and phosphorus, suggesting the presence of a methyl group bound to rhodium, and two doublets at 51.92 and 51.51, consistent with inequivalent methyl groups in a $P(OMe)_2$ ligand. A doublet of doublets is also seen at δ 52.57, which is assigned to coordinated ethylene. The above data are most consistent with the formulation of this major product as $(C_5H_5)Rh[P(O)(OMe)_2](Me)(C_2H_4)$, in which the methyl has migrated to the metal center in an Arbusov rearrangement (eq 6).



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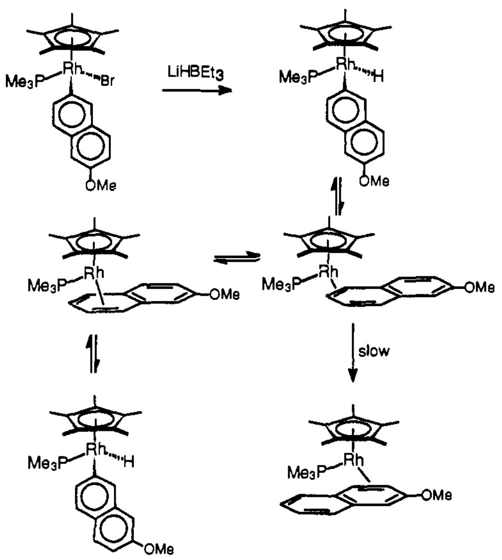
Polycyclic Fused η^2-Arene Studies. In light of the results with naphthalene, substituted naphthalenes and other fused polycyclic aromatics were examined for C–H activation, as summarized in Scheme II. Generally, a hexane solution of phenyl hydride **1** was heated at 60–70 °C with an excess of the polycyclic aromatic for several days. Removal of the solvent under vacuum followed by addition of C_6D_6 permitted examination of the products by NMR spectroscopy. Separation of the metal-containing products from the residual arene was difficult and not always possible, nor was separation of mixtures of isomeric products.

Reaction of **1** with 2-methoxynaphthalene gives a single product assigned as $(C_5Me_5)Rh(PMe_3)[3,4\text{-}\eta^2\text{-}2\text{-methoxynaphthalene}]$. The complex displays two multiplets in the ^1H NMR spectrum at δ 3.043 (td, J = 7.3, 2.4 Hz) and 3.678 (td, J = 7.8, 2.6 Hz) for the η^2-bound double bond and a ^{31}P doublet at δ 0.39 (J = 201 Hz) with a coupling constant typical of a Rh(I) oxidation state in this series of compounds.[15] The presence of four mutually coupled aromatic multiplets (not coupled to the η^2-olefinic hydrogens) in the ^1H–^1H COSY spectrum was used in assigning the geometry of the complex. There was no evidence for a C–H insertion product.

Scheme III



A similar reaction occurs with the symmetric arene 2,6-dimethoxynaphthalene. The single product shows bound η^2-resonances at δ 3.023 (td, J = 7.6, 1.9 Hz) and 3.664 (td, J = 7.8, 2.4 Hz) and a ^{31}P doublet at δ 0.50 (J = 201 Hz), as well as two distinct methoxy resonances.

The formation of the $3,4\text{-}\eta^2$-2-methoxynaphthalene product was shown to be thermodynamic in origin. The complex $(C_5Me_5)Rh(PMe_3)[2\text{-}(6\text{-methoxynaphthyl})]H$ was prepared by reaction of the corresponding aryl Grignard reagent with $(C_5Me_5)Rh(PMe_3)Br_2$ followed by treatment with $LiHB(s\text{-}Bu)_3$. A ^1H NMR spectrum showed not only the formation of this hydride but also an η^2-methoxynaphthalene complex different from that described above. Upon standing for several days, the intensities of the resonances for these complexes were seen to disappear as those for $(C_5Me_5)Rh(PMe_3)[3,4\text{-}\eta^2\text{-}2\text{-methoxynaphthalene}]$ increased. Scheme III shows the pathway proposed for this rearrangment.

Reaction of phenyl hydride **1** with 2-methylnaphthalene gives a more complex mixture of four products, as evidenced by ^{31}P NMR spectroscopy (Scheme II). One of these was identified as the commonly observed thermal decomposition product of **1**, $(C_5Me_5)Rh(PMe_3)_2$, observed at δ −6.11 (d, J = 218 Hz) in 20% yield. The remaining three were present in a 6:1:1 ratio, all with ^{31}P chemical shifts near 1 ppm (±0.4) and J_{Rh-P} of 203–204 Hz, consistent with their formulation as η^2-complexes of 2-methylnaphthalene. The major isomer could be assigned by analysis of the aromatic region of the ^1H–^1H COSY spectrum as $(C_5Me_5)Rh(PMe_3)[3,4\text{-}\eta^2\text{-}2\text{-methylnaphthalene}]$. The remaining two complexes were present in insufficient amounts to permit assignment of all resonances but are assigned as the alternative isomers $(C_5Me_5)Rh(PMe_3)[5,6\text{-}\eta^2\text{-}2\text{-methylnaphthalene}]$ and $(C_5Me_5)Rh(PMe_3)[7,8\text{-}\eta^2\text{-}2\text{-methylnaphthalene}]$.

Several three-ring fused polycyclic aromatics were also examined. Reaction of phenyl hydride **1** with phenanthrene gives a single product in which the metal binds to the central double bond (Scheme II). An X-ray structure of $(C_5Me_5)Rh(PMe_3)(9,10\text{-phenanthrene})$, reported in detail earlier,[12] is shown in Figure 2. The η^2-bound double-bond hydrogens are now equivalent, and the ^1H NMR spectrum shows a simple doublet of doublets at δ 3.560 (J = 8.0, 2.5 Hz). The ^{31}P NMR spectrum shows a doublet at δ 0.31 (J = 201 Hz). The complex is red (as are many of these η^2-arene complexes) with λ_{max} at 325 and 385 nm. The Rh–C14–C15 plane is canted 111° away from the plane of the arene ring, and there is significant lengthening of the coordinated bond C14–C15 (1.428(6) Å) and adjacent bonds C14–C19 (1.469(5) Å) and C15–C16 (1.460(5) Å) compared with the corre-

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[15] Klingert, B.; Werner, H. *Chem. Ber.* **1983**, *116*, 1450–1462.

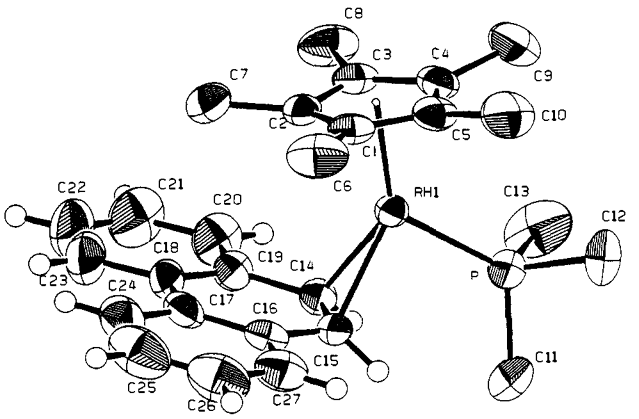
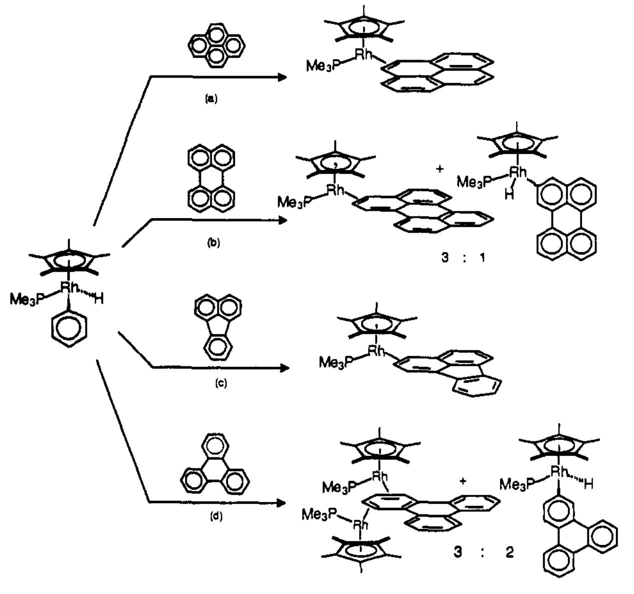


Figure 2. ORTEP drawing of $(C_5Me_5)Rh(PMe_3)(9,10\text{-}\eta^2\text{-phenanthrene})$. Ellipsoids are shown at the 50% probability level. Hydrogens on the C_5Me_5 and PMe_3 ligands have been omitted for clarity. Selected distances (Å): Rh–C14, 2.128(4); Rh–C15, 2.144(4); C14–C15, 1.428(6); C14–C19, 1.469(5); C15–C16, 1.460(5).

Scheme IV



sponding bond distances in free phenanthrene (which are 1.372, 1.390, and 1.390 Å, respectively.[16]

The isomeric fused aromatic anthracene also reacts thermally with **1** to give only an η^2-arene complex. The complexity of the aromatic region of the ^1H spectrum and the inequivalence of the η^2-bound hydrogens (δ 3.260 (m), 3.820 (td, J = 7.4, 1.9 Hz)) indicated that the product was $(C_5Me_5)Rh(PMe_3)(1,2\text{-}\eta^2\text{-anthracene})$ (Scheme II). The ^{31}P NMR spectrum showed only a doublet at δ 0.59 (J = 200 Hz), with no evidence for a C–H addition product. Upon standing in concentrated solution for several weeks, a second product began to appear (~5%) which was assigned as the dinuclear complex $[(C_5Me_5)Rh(PMe_3)]_2(1,2\text{-}\eta^2\text{-}3,4\text{-}\eta^2\text{-anthracene})$ analogous to the dinuclear naphthalene adduct **4**.

The reaction of **1** with fluoranthene was also examined to determine the selectivity for the isolated vs fused six-membered rings. A single product was seen in the ^{31}P NMR spectrum (δ –0.02 (d, J = 199 Hz)), indicating the presence of an η^2-complex. ^1H–^1H COSY NMR spectroscopy was used to assign the product as the adduct in which the metal binds to the 2 and 3 carbons of the ring, i.e. to the fused six-membered ring (Scheme IV(c)).

Reaction of **1** with triphenylene gave a mixture of two compounds in a 3:2 ratio as determined by ^{31}P NMR spectroscopy.

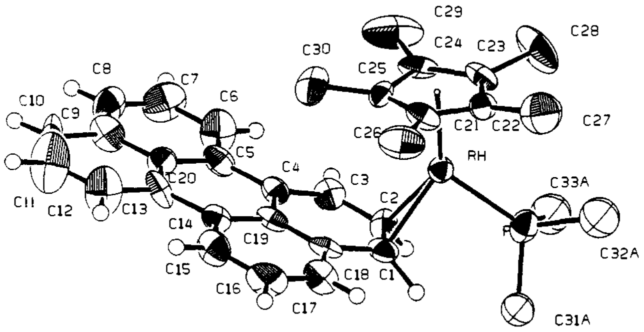


Figure 3. ORTEP drawing of $(C_5Me_5)Rh(PMe_3)(2,3\text{-}\eta^2\text{-perylene})$. Ellipsoids are shown at the 50% probability level. Hydrogens on the C_5Me_5 ligand have been omitted for clarity.

From the chemical shift/coupling constant information, the major product was a Rh(I) η^2-arene complex whereas the minor product was a Rh(III) C–H activation product. The major ^{31}P NMR resonance observed at δ 2.039 showed a Rh–P coupling constant of 209 Hz, which is comparable to that seen in a bis-η^2-arene complex (cf. **4**, $J_{Rh\text{-}P}$ = 210 Hz; $[(C_5Me_5)Rh(PMe_3)]_2(1,2\text{-}\eta^2\text{-}3,4\text{-}\eta^2\text{-anthracene})$, $J_{Rh\text{-}P}$ = 207 Hz). The ^1H NMR spectrum indicated that in this major species the metal was bound asymmetrically to the arene (two distinct Rh–CH resonances are seen at δ 3.648 (t, J = 7.0 Hz) and 3.602 (td, J = 7.0, 2.3 Hz) in C_6D_6 solution), leading to the formulation as $[(C_5Me_5)Rh(PMe_3)]_2(1,2\text{-}\eta^2\text{-}3,4\text{-}\eta^2\text{-triphenylene})$ as shown in Scheme IV(d). The C–H activation product is assigned as being attached at the less hindered 2-position of the ring, since 1-substituted rhodium aryl hydrides have not been previously observed.

Two other fused polycyclic systems were also examined. The reaction of **1** with pyrene gives two products in a 9:1 ratio. The major species is the simple adduct in the central double bond (Scheme IV(a)) on the basis of the single η^2-bound hydrogen resonance (δ 3.827 (dd, J = 7.9, 1.8 Hz)) in the ^1H NMR spectrum and the doublet in the ^{31}P NMR spectrum at δ 0.20 (J = 200 Hz). The minor product was assigned as a dinuclear complex in which two rhodium fragments had bonded to opposite sides of the pyrene ring.

The five-ring arene perylene was also reacted thermally with **1**. The reaction gives a 3:1 mixture of products. The ^{31}P NMR spectrum indicated that the major species was a Rh(I) complex (δ 0.79 (J = 198 Hz)), whereas the minor product was a Rh(III) complex (δ 8.31 (J = 152 Hz)). The Rh(III) complex was easily identified as the C–H activation product formed by insertion into the 2-position of the ring (Scheme IV(b)). The Rh(I) product was identified as the 2,3-η^2-perylene adduct by single-crystal X-ray structure determination (Figure 3). The Rh–C1–C2 plane forms a 111° angle with the planar polycyclic arene ring. Bond lengthening is noticed in coordinated bond C1–C2 (1.45(2) Å) compared with 1.370 Å in free perylene.[16] Adjacent bonds C1–C18 (1.44(2) Å) and C2–C3 (1.43(2) Å) and trans bond C4–C19 (1.44(2) Å) are not lengthened significantly compared to similar bonds in free perylene (which are 1.400, 1.418, and 1.425 Å, respectively). Table II gives atomic coordinates, and Table III gives selected distances and angles.

Discussion

The binding of metals to an isolated double bond of an arene is a fairly well established form of ligation both with single- and multiple-fused aromatics but has often been associated with d^6 and d^{10} fragments.[12,17–19] In the present system thermolysis of phenyl hydride **1** in the presence of excess polycyclic arene in many cases leads to the formation of only one product, the η^2-arene complex, despite the fact that $[(C_5Me_5)Rh(PMe_3)]$ with

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[16] Allinger, N. L.; Sprague, J. T. *J. Am. Chem. Soc.* **1973**, *95*, 3893–3907.

[17] Sweet, J. R.; Graham, W. A. G. *Organometallics* **1983**, *2*, 135–140. Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1987**, *109*, 1883–1885. Harman, W. D.; Sekine, M.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 5725–5731.

Table II. Positional Parameters and B_{eq} for $(C_5Me_5)Rh(PMe_3)(\eta^2\text{-perylene})$

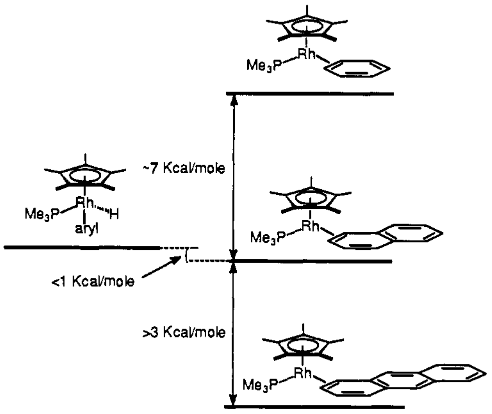
atom	x	y	z	B_{eq} (Å^2)
Rh	0.35722(4)	0.0099(1)	0.66496(6)	2.66(4)
P	0.3429(1)	0.2266(4)	0.6652(2)	3.7(2)
C1	0.3841(5)	0.035(1)	0.5672(7)	3.2(8)
C2	0.3400(5)	0.012(2)	0.5442(6)	3.9(7)
C3	0.3261(4)	–0.112(1)	0.5135(7)	3.3(7)
C4	0.3516(5)	–0.211(1)	0.4998(7)	2.9(7)
C5	0.3362(5)	–0.337(1)	0.4647(7)	3.5(8)
C6	0.2954(5)	–0.369(2)	0.449(1)	6(1)
C7	0.2804(5)	–0.489(2)	0.4157(9)	6(1)
C8	0.3078(7)	–0.577(2)	0.3956(9)	5(1)
C9	0.3505(5)	–0.552(2)	0.4124(9)	4.1(9)
C10	0.3791(7)	–0.642(2)	0.3927(9)	6(1)
C11	0.4201(7)	–0.620(2)	0.409(1)	8(1)
C12	0.4344(5)	–0.500(2)	0.442(1)	7(1)
C13	0.4086(5)	–0.408(2)	0.4636(8)	3.8(9)
C14	0.4242(5)	–0.283(1)	0.5002(7)	2.8(7)
C15	0.4666(5)	–0.257(2)	0.5151(8)	4.3(8)
C16	0.4814(5)	–0.134(2)	0.5457(9)	5(1)
C17	0.4537(5)	–0.045(1)	0.5636(7)	4.1(8)
C18	0.4113(5)	–0.067(2)	0.5506(7)	3.2(8)
C19	0.3955(5)	–0.187(2)	0.5168(7)	2.9(7)
C20	0.3654(6)	–0.432(1)	0.4467(8)	3.3(3)
C21	0.4008(5)	–0.114(1)	0.7489(8)	3.2(7)
C22	0.3790(5)	–0.031(1)	0.7871(7)	3.3(8)
C23	0.3356(5)	–0.062(1)	0.7688(8)	3.6(8)
C24	0.3318(5)	–0.170(1)	0.7194(8)	3.6(8)
C25	0.3716(5)	–0.200(1)	0.7046(7)	2.6(7)
C26	0.4467(6)	–0.122(2)	0.7549(8)	6(1)
C27	0.3980(6)	0.061(2)	0.8503(9)	8(1)
C28	0.3021(5)	–0.007(2)	0.8060(8)	8(1)
C29	0.2948(6)	–0.248(2)	0.6909(9)	8(1)
C30	0.3831(5)	–0.323(1)	0.6672(8)	5.6(9)
C31A	0.3617(7)	0.337(2)	0.599(1)	4.2(5)
C31B	0.309(2)	0.285(5)	0.731(3)	5(1)
C32A	0.3555(8)	0.325(2)	0.750(1)	6.1(6)
C32B	0.321(2)	0.316(5)	0.588(3)	6(1)
C33A	0.2876(8)	0.267(2)	0.640(1)	6.1(6)
C33B	0.394(2)	0.303(6)	0.704(3)	7(2)
O1	1.0000	0.018(5)	1/4	32(2)
C34	0.997(1)	0.092(4)	0.186(2)	26(2)
C35	0.991(1)	0.227(4)	0.212(2)	24(2)

Table III. Selected Distances (Å) and Angles (deg) for $(C_5Me_5)Rh(PMe_3)(\eta^2\text{-perylene})$

	Distances		
Rh–P	2.245(4)	C4–C19	1.44(2)
Rh–C1	2.13(1)	C13–C14	1.48(2)
Rh–C2	2.16(1)	C14–C15	1.40(2)
C1–C2	1.45(2)	C14–C19	1.42(2)
C1–C18	1.43(2)	C15–C16	1.41(2)
C2–C3	1.42(2)	C16–C17	1.37(2)
C3–C4	1.36(2)	C17–C18	1.39(2)
C4–C5	1.47(2)	C18–C19	1.42(2)
	Angles		
P–Rh–C1	90.3(4)	Rh–C1–C18	117.1(9)
P–Rh–C2	88.5(4)	C2–C1–C18	117(1)
C1–Rh–C2	39.6(5)	Rh–C2–C1	69.2(7)
Rh–C1–C2	71.2(7)	Rh–C2–C3	113(1)

its d^8 configuration has been demonstrated to be a potent activator of both alkane and arene C–H bonds. These changes are most easily followed by ^{31}P NMR spectroscopy, in which the downfield resonance for the Rh(III) complex **1** with a small J_{P-Rh} of ~150 Hz is seen to move upfield for a Rh(I) η^2-arene complex as J_{P-Rh} increases to ~200 Hz. In several instances, C–H oxidative addition products can also be seen, which have been shown to be in equilibrium ($\tau_{1/2}$ ~ 1 s) with the η^2-complexes for several arenes.

Scheme V



From the above studies, the unique feature of the polycyclic aromatics lies in the stability of the η^2-complex relative to the aryl hydride complex. For benzene, the η^2-complex is destabilized relative to the η^2-naphthalene complex, whereas the C–H activation complexes both have energies comparable to that of the η^2-naphthalene complex. On the other hand, the η^2-complex of anthracene is much more stable than its C–H activation adduct, as shown in Scheme V. *It is becoming clear that it is the energy of the η^2-complex that determines whether or not C–H oxidative addition is observed and that the C–H, M–C, and M–H bond strengths should not be the only factors considered.* The origin of this destabilization can be directly attributed to the interruption of the resonance of the aromatic ring, which is reduced in the naphthalene complex relative to benzene. Table IV summarizes calculations of the energies of the free and bound arene in terms of the p-orbital interaction integral β.[20] The balance point for C–H activation vs η^2-coordination occurs at $\Delta E_r \cong 1.25\beta$ for the C_5Me_5 complexes. Values larger than this give C–H activation only, and smaller values result in only η^2-arene complexation (vide infra). Other examples support this hypothesis, as outlined in Schemes II and IV and discussed below.[21]

With 2-methoxynaphthalene, only the η^2-complex is observed in the 3,4-position of the ring. No C–H activation is seen. In this example, the loss of resonance energy is minimal ($\Delta E_r = 1.04\beta$, Table IV), so that the aromatic ligand behaves as an olefin! The reactivity is similar to that of styrene, which also forms only an η^2-complex with the vinylic portion of the molecule. Other simple arene selectivities (thermodynamic, since the arenes exchange under the reaction conditions) are indicated in Scheme II. With phenanthrene and anthracene, only a single η^2-complex is seen, again in accord with the ΔE_r calculations in Table IV. Notice that other possible coordination isomers have higher ΔE_r values and hence are not observed under the experimental conditions which lead to thermodynamic products. These ΔE_r values therefore serve in a qualitative predictive capacity, but actual free energy differences cannot be calculated from them.

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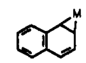
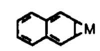
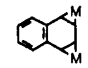
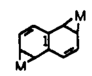
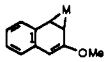
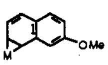
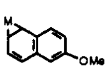
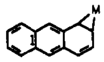
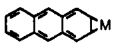
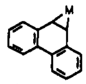
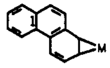
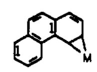
(18) (a) van der Heijden, H.; Orpen, A. G.; Pasman, P. *J. Chem. Soc., Chem. Commun.* **1985**, 1576–1578. (b) Neithamer, D. R.; Parkanyi, L.; Mitchell, J. F.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1988**, *110*, 4421–4423. (c) Harman, W. D.; Taube, H. *Inorg. Chem.* **1987**, *26*, 2917–2918. (d) Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 7555–7556. (e) Brauer, D. J.; Kruger, C. *Inorg. Chem.* **1977**, *16*, 884–891.

(19) Turner, R. W.; Amma, E. L. *J. Am. Chem. Soc.* **1966**, *88*, 1877–1882. Turner, R. W.; Amma, E. L. *J. Chem. Soc.* **1966**, *88*, 3243–4247. Browning, J.; Green, M.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1974**, 97–101.

(20) This method of analyzing π-bonding energies has been presented previously in ref 18e. A similar argument was used by Hodges and Garnett (*J. Phys. Chem.* **1969**, *73*, 1525) in their pioneering studies of H/D exchange in aromatics catalyzed by Pt(II). They showed that the activation energy for exchange is lower for naphthalene than for benzene and that exchange occurred predominantly in certain positions. They argued that "the intermediate π-complex is formed...preferentially with the bond with lowest double bond localization energy."

(21) Harman has proposed loss of resonance energy to be responsible for the shift in the keto–enol equilibrium upon η^2-coordination of phenol. See: Kopach, M. E.; Hipple, W. G.; Harman, W. D. *J. Am. Chem. Soc.* **1992**, *114*, 1736–1740.

Table IV. Resonance Energies for η^2-Arene Complexes (in Units of β)

complex	resonance energy of free arene	resonance energy of η^2-arene	$\Delta E_r\ \beta$ (kcal/mol)[a]
	2	0.47	1.53 (30.6)
	3.68	2.42	**1.26 (25.2)**
	3.68	1.95	1.73 (34.6)
	3.68	2.00	**1.68 (33.6)**
	3.68	0.99	2.69 (53.8)
	4.43	3.39	**1.04 (20.8)**
	4.43	3.19	1.24 (24.8)
	4.43	3.14	1.29 (25.8)
	5.31	4.11	**1.20 (24.0)**
	5.31	3.53	1.82 (36.4)
	5.45	4.38	**1.07 (21.4)**
	5.45	4.13	1.32 (26.4)
	5.45	4.11	1.34 (26.8)

[a] Bold type indicates the most stable isomer.

With 2-methylnaphthalene, however, three different η^2-complexes are observed, since they all have comparable ΔE_r energies (the same as naphthalene). Curiously, however, no C–H insertion is seen with this substrate, despite the fact that the ΔE_r values are the same as those of naphthalene. This observation requires that the free energies of these aryl hydride complexes be much higher than that of the η^2-complex, unlike the parent naphthalene case. It has been previously established in this system that electron-withdrawing substituents on benzene lead to more stable aryl hydride complexes and that electron-donating substituents such as methyl destabilize the aryl hydride complexes.[3]

The effect of electron-withdrawing substituents can also be seen in comparison of the reactions of 1,4-bis(trifluoromethyl)benzene. Electron-rich metal centers such as [$(C_5Me_5)Rh(PMe_3)$] and [$(C_5H_5)Ir(PMe_3)$] react with this substrate to give C–H insertion products exclusively. Upon using the slightly less electron rich complex [$(C_5H_5)Rh(PMe_3)$], an equilibrium is observed between the C–H insertion product and the η^2-arene adduct, with the latter complex being slightly favored (0.9 kcal/mol). Use of 1,3-bis(trifluoromethyl)benzene also gives a mixture of C–H insertion and η^2-products, although now the C–H insertion product is favored (by 1.8 kcal/mol). This shift of 2.7 kcal compared to the 1,4-substituted arene is significant, indicating that the presence of an equilibrium in the case of 1,4-bis(trifluoromethyl)benzene is only partially attributable to steric destabilization of the C–H insertion complex by an ortho CF_3 group. The electronic effect of the two CF_3 groups in 1,3-bis(trifluoromethyl)benzene must play a role in stabilizing the η^2-complex.

If the strong σ-donor PMe_3 ligand is replaced with the weaker donor $P(OMe)_3$, the only product from reaction with the bis(trifluoromethyl)benzene is the η^2-arene complex. The phosphonate complex that is also observed is similar to that seen upon thermolysis of $\{(C_5H_5)Rh[P(OMe)_3]_2(CH_3)\}I$.[22] The electron-deficient arene C_6F_6 was also seen to readily form η^2-arene complexes with these types of metal fragments.[10] Consequently, electron-withdrawing groups can be seen to stabilize η^2-arene complexes, with the electron density at the metal center mediating the balance between C–H oxidative addition and η^2-coordination. The earlier observation of an η^2-complex with the electron-rich arene *p*-di-*tert*-butylbenzene, $(C_5Me_5)Rh(PMe_3)[\eta^2\text{-}1,4\text{-}C_6H_4(t\text{-}Bu)_2]$, can be accounted for in terms of a destabilization of $(C_5Me_5)Rh(PMe_3)[2,5\text{-}C_6H_3(t\text{-}Bu)_2]H$ due to steric interference of the *tert*-butyl groups with the metal. The η^2-complex was, in fact, labile even at –10 °C, as demonstrated by spin saturation transfer with free ligand in solution.[3]

The 2-methoxynaphthalene derivative also offered the opportunity to study the kinetic isomers of the reaction. Preparation of $(C_5Me_5)Rh(PMe_3)[6\text{-}(2\text{-methoxynaphthalene})]H$ was performed by way of hydridic reduction of the corresponding bromide complex. The initially formed aryl hydride complex can rapidly isomerize between four species by way of rhodium hydride $\rightleftharpoons$ η^2-arene equilibria, as shown in Scheme III. This result is to be expected, as the ΔE_r values for these η^2-complexes from Table IV are 1.24 and 1.29. Over several days time at room temperature, these isomers were converted into the single more stable thermodynamically preferred 3,4-isomer. This isomerization required migration past the carbon at the ring juncture and consequently occurs more slowly.

Similar rearrangements have been probed in the parent naphthalene system.[13] Reaction of the complex $(C_5Me_5)Rh(PMe_3)(2\text{-naphthyl})Br$ with $LiDBEt_3$ gives a mixture of four isomers in which the deuterium has scrambled over the two possible 2-naphthyl derivatives and two possible η^2-isomers. Slowly, the initial isomers equilibrate with the four isomers in which the rhodium has migrated across to the unsubstituted ring. Since this rearrangement occurs more rapidly than the rate at which naphthalene dissociates from $(C_5Me_5)Rh(PMe_3)(\eta^2\text{-naphthalene})$, the reaction must be intramolecular.

Further heating of the reaction of $(C_5Me_5)Rh(PMe_3)(Ph)H$ with naphthalene ultimately leads to a new thermodynamically preferred product in which *two* rhodiums are attached to the aromatic ligand. Periodic removal of naphthalene helps to shift this equilibrium toward the binuclear adduct, allowing its isolation and characterization in pure form. COSY NMR studies indicate that both metals are on one aromatic ring. The X-ray structure confirms that both metals are on the same aromatic ring but on opposite faces.[13] The preference for keeping the aromatic ring pointing up toward the C_5Me_5 ring can also be seen here, as in the phenanthrene complex (Figure 2).[16] It is worth noting that the binding of two metals to an aromatic ring in an η^2–η^2 fashion has been seen in several other cases, and a review of these has recently appeared.[23]

The ΔE_r calculations for the possible binuclear adducts given in Table IV are in agreement with the observed isomer. While the large value of ΔE_r (1.68) would suggest that only C–H activation should be observed, this energy cost should be divided over two metal–arene interactions, giving a ΔE_r of 0.84 per metal, which is well within the η^2-regime. In essence, the binding of one metal to naphthalene leaves behind a styrene moiety, which is very susceptible to coordination by a second metal.

In the case of phenanthrene and perylene, the η^2-complexes were crystallized and structurally characterized (Figure 2 and 3). Three structural features are to be noted: (1) only two carbons interact with the metal, (2) the arene ring is oriented away from

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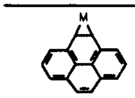
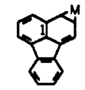
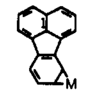
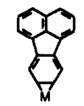
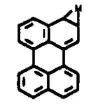
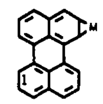
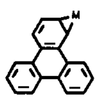
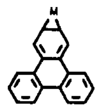
Table V. Resonance Energies for η^2-Arene Complexes (in Units of β)

complex	resonance energy of free arene	resonance energy of η^2-arene	$\Delta E_r\ \beta$ (kcal/mol)[a]
	6.51	5.45	**1.06 (21.2)**
	6.51	5.09	1.42 (28.4)
	6.50	5.22	**1.28 (25.6)**
	6.50	5.03	1.46 (29.2)
	6.50	4.97	1.53 (30.6)
	8.25	7.02	**1.23 (24.6)**
	8.25	6.68	1.57 (31.4)
	7.27	5.89	**1.38 (27.6)**
	7.27	5.68	1.60 (32.0)

[a] Bold type indicates the most stable isomer.

the phosphine and toward the C_5Me_5 ring, and (3) the ring plane is canted characteristically at 111° to the plane containing Rh and the coordinated carbon atoms, a very similar value to that found in $(C_5H_5)Rh(PMe_3)(\eta^2\text{-}C_6F_6)$, viz. 108°.[6] The alternative orientation would cause steric interference of the aromatic with the trimethylphosphine. The UV-visible spectra of these red complexes are interpreted in terms of metal to ligand π^* charge-transfer bands.

A variety of other larger fused polycyclic aromatics have also been examined. These include pyrene, perylene, fluoranthene, and triphenylene. These studies indicate that in most cases η^2-arene complexation is strongly preferred but that in others C–H activation also occurs (Scheme IV). As in the earlier cases, examination of the resonance energy costs based on simple Hückel energies allows one to account for the observations. The results of these calculations are summarized in Table V.

There are several points worth noting here. First, the observations with pyrene (only η^2-complex) and perylene (mixture of η^2-complex and C–H insertion complex) are in agreement with the calculated predictions based on $\Delta E_r = 1.25$ as the break point. However, with fluoranthene, one would have predicted the observation of significant quantities of the C–H activation adduct at the 2-position (with no ortho substituents), but no such product is seen. It is possible that the electronic effects induced by the presence of C–C bonds in the α-positions of the naphthalene nucleus of this complex raise the energy of the C–H insertion product, as occurs with 2-methylnaphthalene. Second, the η^2-isomers observed with pyrene, perylene, and fluoranthene are in accord with the lowest ΔE_r values in Table V. With triphenylene, however, none of the mononuclear 1,2-η^2-isomer is seen. This observation could be reconciled in that the ΔE_r value for the η^2-adduct is above the balance point (1.38). On the other hand, the bis-η^2-complex is stable with respect to the corresponding C–H activation product.

Conclusions

In summary, the chemistry of a variety of rhdoium complexes has been explored with regard to their fundamental interactions with hydrocarbons and their mechanisms of reactions. Several factors that contribute to the stability of η^2-arene complexation relative to C–H bond activation have been determined. The phenomenon of tautomerism involving hydrogen transfer between metal and ligand yielding alternative η^2- and η^1-coordination modes has proved fundamental to recent progress in coordination chemistry. Thus equilibria between pairs such as $M(\eta^2\text{-}H_2)/M(H)_2$, $M(\eta^2\text{-alkyl})(\text{agostic})/M(H)(\eta^1\text{-alkyl})$, or $M(\eta^2\text{-}HSiR_3)/M(H)(SiR_3)$ can be tuned by suitable choice of metal and ligands. We have now demonstrated that equilibria between $M(\eta^2\text{-arene})$ and $M(\text{aryl})H$ complexes may also be tuned by variation of metal and ancillary ligands. In this special case, the arene itself has a major impact on the position of equilibrium. Specific comparisons showing this shift favoring η^2-arene complexes are seen with the interactions of (1) $p\text{-}C_6H_4(CF_3)_2$ vs C_6H_6 with $[(C_5H_5)Rh(PMe_3)]$, (2) $p\text{-}C_6H_4(CF_3)_2$ with $[(C_5H_5)Rh(PMe_3)]$ vs $[(C_5Me_5)Rh(PMe_3)]$, and (3) 2-methoxynaphthalene vs naphthlene with $[(C_5Me_5)Rh(PMe_3)]$.

Experimental Section

General Procedures. All manipulations were performed under an inert atmosphere of nitrogen or on a high-vacuum line with the use of Schlenk techniques. Tetrahydrofuran (THF) and hexane (olefin free) were distilled from dark-puple solutions of sodium–benzophenone ketyl under vacuum. Before distillation, hexane was stirred for 48 h over two portions of concentrated H_2SO_4, washed with saturated $KMnO_4$ in 10% H_2SO_4, two portions of H_2O, one portion of saturated Na_2CO_3, and two portions of H_2O, and then dried over anhydrous $CaCl_2$. All arenes, aryl halides, hexamethyl Dewar benzene, and L-Selectride (lithium tri-*sec*-butylborohydride) were purchased from Aldrich Chemical Co. Magnesium turnings were obtained from Reade Manufacturing Corp. $(C_5Me_5)Rh(PMe_3)Br_2$ and $(C_5Me_5)Rh(PMe_3)(Ph)H$ were prepared according to the procedures of Kang[24] and Jones and Feher.[3] $(C_5H_5)Rh(PMe_3)(C_2H_4)$,[25] $(C_5H_5)Rh[P(OMe)_3](C_2H_4)$,[26] and $(C_5H_5)Ir(PMe_3)H_2$[27] were prepared as previously described.

^1H (400 and 300 MHz), ^{31}P (162 and 121 MHz), and ^{13}C NMR (100 and 75 MHz) NMR spectra were recorded on Bruker AMX-400, Bruker MSL-300, or GE QE-300 spectrometers. Both low- and high-temperature NMR experiments were regulated by a Bruker BVT-100 temperature control unit (±0.1 °C). Temperatures were calibrated with use of standard methanol (−70 to 30 °C) and ethylene glycol (20 to 70 °C) calibration samples. ^1H NMR shifts were measured relative to residual ^1H resonances in the deuterated solvents C_6D_6 (δ 7.150), C_6D_{12} (δ 1.380), and acetone-d_6 (δ 2.040). ^{31}P NMR spectra were reported in units of δ (chemical shifts are referred to external 10% H_3PO_4 at δ 0.0 ppm). ^{13}C NMR spectra were measured relative to the deuterated solvent resonance (C_6D_6, δ 128.00; C_6D_{12}, δ 26.40). C_6D_6 and C_6D_{12} were purchased from MSD Isotope Merck Chemical Division Company and were vacuum-distilled from potassium–benzophenone prior to use. Acetone-d_6 was purchased from MSD Co. and was dried over CaH_2. Elemental analyses were performed by Desert Analytics-Organic Microanalysis Laboratory. An Enraf-Nonius CAD4 diffractometer was used for X-ray crystal structure determinations. Simple Hückel calculations were done by diagonalization of the appropriate unit matrices using the program ASYST.[28]

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Solutions for photolysis (typically 2–4 mL) were made up in small Pyrex ampules fitted with Tefon stopcocks. They were degassed with three freeze–pump–thaw cycles and then back-filled with argon before irradiation with an Applied Photophysics high-pressure mercury arc lamp (250 W).

Preparation of Bromide-Containing Grignard Reagents. For (2-naphthyl)MgBr in THF, anhydrous THF (15 mL) was transferred into a 100-mL flask containing Mg turnings (0.90 g, 0.037 mol). 2-Bromonaphthalene (2.7 g, 0.013 mol) in 15 mL of THF was added over a period of 1 h under N_2 at room temperature. The mixture was stirred for 24 h at 24 °C. Filtration gave a brown-yellow THF solution of (2-naphthyl)MgBr. The solution was standardized with 1.06 M *tert*-butyl alcohol/toluene in the presence of 1,10-phenanthroline before use. [2-(6-Methoxy)naphthyl]MgBr was prepared in an analogous fashion.

Preparation of $(C_5Me_5)Rh(PMe_3)(2\text{-naphthyl})Br$. $(C_5Me_5)Rh(PMe_3)Br_2$ (0.120 g, 0.25 mmol) was dissolved in 15 mL of anhydrous THF under nitrogen. 2-Naphthyl magnesium bromide/THF (3.4 mL, 0.32 M, 1.09 mmol) was added drop by drop at room temperature over 10 min with a syringe. The dark-red solution turned orange gradually. The solution was stirred for 2 h, and 0.8 mL of a saturated solution of NH_4Br was then added to quench the reaction. The solvent was removed under reduced pressure and the product extracted in methylene chloride. The red-orange solution was reduced to 0.5 mL and introduced onto a silica gel TLC plate. The first orange band that eluted with a 2% THF/CH_2Cl_2 solvent system was the desired product. Orange crystals were recrystallized from CH_2Cl_2/hexane in 42% yield. Anal. Calcd for $C_{23}H_{31}BrPRh$: C, 53.00; H, 6.00. Found: C, 53.01; H, 5.92. The molecule shows evidence for hindered rotation about the Rh–naphthyl bond.[29] ^{1}H NMR (C_6D_6, 25 °C): δ 1.058 (d, J = 10.3 Hz, 9 H), 1.393 (d, J = 2.8 Hz, 15 H), 7.26 (m, 1 H), 7.59 (br d, 2 H), 7.73 (br s, 2 H). ^{1}H NMR [$(CD_3)_2CO$]: δ 1.431 (d, J = 10.6 Hz, 9 H), 1.642 (d, J = 2.8 Hz, 15 H), 7.222 (t, J = 7.2 Hz, 1 H), 7.300 (t, J = 7.2 Hz, 1 H), 7.317 (br s), 7.605 (br d), 7.684 (d, J = 7.9 Hz, 1 H). At −62 °C, rotamer A: δ 1.407 (d, J = 10.7 Hz, 9 H), 1.595 (d, J = 2.7 Hz, 15 H), 7.235 (m, 1 H), 7.312 (m, 1 H), 7.368 (d, J = 8.5 Hz, 1 H), 7.657 (s, 1 H), 7.709 (d, J = 7.9 Hz, 1 H), 7.743 (d, J = 8.1 Hz, 1 H), 8.160 (d, J = 8.4 Hz, 1 H). Rotamer B: δ 1.369 (d, J = 10.7 Hz, 9 H), 1.601 (d, J = 2.6 Hz, 15 H), 7.235 (m, 1 H), 7.312 (m, 1 H), 7.403 (d, J = 8.2 Hz, 1 H), 7.488 (d, J = 8.2 Hz, 1 H), 7.562 (d, J = 8.2 Hz, 1 H), 7.709 (d, J = 7.9 Hz, 1 H), 8.382 (s, 1 H). At 62 °C δ 1.448 (d, J = 10.8 Hz, 9 H), 1.657 (d, J = 2.8 Hz, 15 H), 7.212 (dt, J = 7.1, 1.2 Hz, 1 H), 7.289 (dt, J = 7.4, 1.3 Hz, 1 H), 7.395 (d, J = 8.4 Hz, 1 H), 7.601 (d, J = 7.8 Hz, 1 H), 7.671 (d, J = 8.1 Hz, 1 H). Slight temperature-dependent chemical shift changes were seen here.

Reduction of $(C_5Me_5)Rh(PMe_3)(2\text{-naphthyl})Br$ by L-Selectride. $(C_5Me_5)Rh(PMe_3)(2\text{-naphthyl})Br$ (0.021 g, 0.040 mmol) was dissolved in 5 mL of THF. A THF solution (0.15 mL, 1 M) of lithium tri-*sec*-butylborohydride (0.15 mmol) was added dropwise via syringe. The solution was stirred for 30 min at room temperature. The solvent was removed under vacuum. ^{1}H NMR and ^{31}P NMR (C_6D_6) spectra showed a mixture of η^2-arene and naphthyl hydride complexes in a ratio of 2:1. Attempts at flash chromatography on silica gel resulted in decomposition.

Reaction of $(C_5Me_5)Rh(PMe_3)(Ph)H$ with Naphthalene. **1** (0.020 g, 0.051 mmol) was dissolved in 4 mL of hexane and an excess of naphthalene added (>10 equiv). The reaction was carried out in a glass ampule at 60 °C for 24 h. The solvent was then removed and free naphthalene removed by sublimation on a vacuum line. The η^2-naphthalene and the naphthyl hydride complexes were formed in a 2:1 ratio in a combined yield of about 100% (0.022 g). For $(C_5Me_5)Rh(PMe_3)(\eta^2\text{-naphthalene})$, ^{1}H NMR ($C_6D_{12}$): δ 1.180 (d, J = 8.0 Hz, 9 H), 1.301 (d, J = 2.6 Hz, 15 H), 3.213 (td, J = 7.4, 2.5 Hz, 1 H), 3.629 (td, J = 7.4, 2.5 Hz, 1 H), 6.564 (d, J = 0.5 Hz, 1 H), 6.570 (dd, J = 4.5, 0.5 Hz, 1 H), 6.889 (t, J = 7.5 Hz, 1 H), 7.041 (t, J = 7.5 Hz, 1 H), 7.109 (d, J = 7.7 Hz, 1 H), 7.275 (d, J = 7.7 Hz, 1 H). ^{31}P{^{1}H} NMR (C_6D_{12}): δ 0.66 (d, J = 203 Hz). ^{13}C{^{1}H} NMR (C_6D_6): δ 9.77 (s, C_5Me_5), 16.13 (d, J = 25.4 Hz, PMe_3), 43.18 (d, J = 13.1 Hz, η^2-CH), 44.39 (d, J = 14.1 Hz, η^2-CH), 95.22 (t, J = 3.4 Hz, C_5Me_5), 124.78 (s, CH), 125.65 (s, CH), 126.00 (s, CH), 126.93 (s, CH), 128.47 (s, CH), 132.41 (s, C), 142.39 (s, C). For $(C_5Me_5)Rh(PMe_3)(2\text{-naphthyl})H$, ^{1}H NMR ($C_6D_{12}$): δ −13.549 (dd, J = 49.8, 32.3 Hz, 1 H), 1.080 (d, J = 8.0 Hz, 9 H), 1.814 (d, J = 1.2 Hz, 15 H), 7.047 (t, J = 8.2 Hz, 1 H), 7.127 (t, J = 7.5 Hz, 1 H), 7.188 (t, J = 8.2 Hz, 1 H), 7.407 (d, J = 8.1 Hz, 1 H), 7.456 (d, J = 8.2 Hz, 1 H), 7.493 (d, J = 8.1 Hz, 1 H), 7.694 (s, 1 H). ^{31}P{^{1}H} NMR (C_6D_{12}): δ 7.63 (d, J = 155 Hz). ^{13}C{^{1}H} NMR (C_6D_6): δ 10.71 (s, C_5Me_5), 18.87 (d, J = 32.1 Hz, PMe_3), 97.57 (t, J = 3.6 Hz, C_5Me_5).

Reductive Elimination of Naphthalene. A solution of $(C_5Me_5)Rh(PMe_3)(2\text{-naphthyl})H$ (~0.020 g, 0.045 mmol), freshly prepared by reduction of $(C_5Me_5)Rh(PMe_3)(2\text{-naphthyl})Br$ with LiB(*s*-Bu)$_3$H, in 0.4 mL of C_6D_6 was placed in an NMR tube fitted with a vacuum adapter and sealed under ~600 mmHg of nitrogen. The kinetics of naphthalene loss was measured at 51 °C by monitoring the decrease of the singlet resonance at δ 8.109. The observed rate constant for reductive elimination of naphthalene from $(C_5Me_5)Rh(PMe_3)(2\text{-naphthyl})H$ was determined as 5.1×10^{-5} s^{-1} from a plot of $\ln[C/C_0]$ vs time.

Preparation of $(C_5Me_5)Rh(PMe_3)[3,4\text{-}\eta^2\text{-2-methoxynaphthalene}]$. $(C_5Me_5)Rh(PMe_3)(Ph)H$ (0.130 g, 0.33 mmol) and 4 equiv of 2-methoxynaphthalene (0.22 g) in hexane (10 mL) were sealed in a 50-mL ampule attached to a Teflon stopcock. The mixture was stirred for 48 h at 60 °C. The reaction was quenched in an ice–water bath, and the deep-red solution was evaporated (25 °C, 10^{-4} mmHg). The residue was extracted with hexane and filtered through a fine-fritted funnel to remove free 2-methoxynaphthalene ligand. The crude product is very clean except for a small amount of free ligand. ^{1}H NMR (C_6D_{12}): δ 1.187 (d, J = 8.1 Hz, 9 H), 1.310 (d, J = 2.6 Hz, 15 H), 3.043 (td, J = 7.3, 2.4 Hz, 1 H), 3.678 (td, J = 7.8, 2.6 Hz, 1 H), 3.721 (s, 3 H), 5.75 (s, 1 H), 6.848 (t, J = 7.4 Hz, 1 H), 6.912 (t, J = 7.4 Hz, 1 H), 7.029 (d, J = 7.2 Hz, 1 H), 7.218 (d, J = 7.5 Hz, 1 H). ^{31}P{^{1}H} NMR (C_6D_{12}): δ 0.39 (d, J = 201 Hz). ^{13}C{^{1}H} NMR (C_6D_6): δ 9.49 (s, C_5Me_5), 15.93 (d, J = 25.5 Hz, PMe_3), 40.31 (dd, J = 14.1, 1.6 Hz, η^2-CH), 45.31 (dd, J = 14.4, 1.6 Hz, η^2-CH), 53.98 (s, OMe), 92.59 (s, CH), 95.32 (t, J = 3.5 Hz, C_5Me_5), 123.20 (s, CH), 123.32, (s, CH), 125.65 (s, CH), 127.67 (s, CH), 133.74 (s, C), 138.70 (s, C), 165.31 (s, C(OMe)).

Preparation of $(C_5Me_5)Rh(PMe_3)[2\text{-(6-methoxynaphthyl)}]Br$. $(C_5Me_5)Rh(PMe_3)Br_2$ (0.152 g, 0.32 mmol) was allowed to react with [2-(6-methoxynaphthyl)]MgBr/THF (0.385 mmol) in THF (ca. 30 mL) at room temperature for 3 h. The reaction was quenched with 1 mL of NH_4Br/H_2O saturated solution. The residue was chromatographed on a thin-layer silica gel plate (2% THF/CH_2Cl_2) to give an orange band containing the desired product $(C_5Me_5)Rh(PMe_3)[2\text{-(6-methoxynaphthyl)}]Br$. Recrystallization afforded orange crystals in 51% yield. Anal. Calcd for $C_{24}H_{33}BrOPRh$: C, 52.29; H, 6.03. Found: C, 52.67; H, 6.04. ^{1}H NMR (C_6D_6): δ 1.085 (d, J = 10.3 Hz, 9 H), 1.418 (d, J = 2.8 Hz, 15 H), 3.443 (s, 3 H), 7.0–7.6 (br), 8.83 (br), 9.03 (br s). At −20 °C, ^{1}H NMR ($(CD_3)_2CO$) showed two rotamers in a 1.4:1 ratio. Rotamer A: δ 1.409 (d, J = 10.9 Hz, 9 H), 1.608 (d, J = 2.6 Hz, 15 H), 3.829 (s, 3 H), 6.944 (d, J = 9.0 Hz, 1 H), 7.085 (s, 1 H), 7.303 (d, J = 9.0 Hz, 1 H), 7.543 (s, 1 H), 7.603 (d, J = 8.9 Hz, 1 H), 8.122 (d, J = 8.4 Hz, 1 H). Rotamer B: δ 1.381 (d, J = 11.1 Hz, 9 H), 1.608 (d, J = 2.6 Hz, 15 H), 3.817 (s, 3 H), 6.944 (d, J = 9.0 Hz, 1 H), 7.085 (s, 1 H), 7.323 (d, J = 7.7 Hz, 1 H), 7.411 (d, J = 8.2 Hz, 1 H), 7.483 (d, J = 8.9 Hz, 1 H), 8.317 (s, 1 H).

Reduction of $(C_5Me_5)Rh(PMe_3)[2\text{-(6-methoxynaphthyl)}]Br$ by L-Selectride. $(C_5Me_5)Rh(PMe_3)[2\text{-(6-methoxynaphthyl)}]Br$ (0.020 g, 0.036 mmol) was dissolved in 5 mL of THF. To this solution was added 3 equiv of LiB(*s*-Bu)$_3$H (0.11 mL of 1 M solution in THF). After the reaction mixture was stirred for 3 h, the THF solvent was removed and replaced by C_6D_{12}. A ^{1}H NMR spectrum of this sample showed that ~50% of the starting material (δ 1.610 (d, J = 2.5 Hz, 15 H), 1.235 (d, J = 8.4 Hz, PMe_3), 8.392 (s, 1 H), 8.176 (d, J = 8.3 Hz, 1 H), 3.754 (s, OMe)) remained. Two of the new products were identified as the known complexes $(C_5Me_5)Rh(PMe_3)[3,4\text{-}\eta^2\text{-2-methoxynaphthalene}]$ and $(C_5Me_5)Rh(PMe_3)H_2$ (δ 1.987 (s, 15 H), −14.102 (dd, J = 43.5, 28.7 Hz, 2 H)). A new hydride, assigned as $(C_5Me_5)Rh(PMe_3)[2\text{-(6-methoxynaphthyl)}]H$ (δ 1.814 (s, 15 H), −12.509 (dd, J = 48.6, 21 Hz, 1 H). ^{31}P{^{1}H} NMR: δ 5.94 (d, J = 145.3 Hz)), and a new η^2-complex $(C_5Me_5)Rh(PMe_3)[5,6\text{-}\eta^2\text{-2-methoxynaphthalene}]$ (^{31}P{^{1}H} NMR: δ 0.54 (d, J = 204 Hz)) were also observed. The intensity of the 3,4-η^2-complex was observed to increase over 3 days as the amounts of the other complexes decreased.

Preparation of $(C_5Me_5)Rh(PMe_3)[3,4\text{-}\eta^2\text{-2,6-dimethoxynaphthalene}]$. 2,6-Dimethoxynaphthalene (0.080 g, 0.425 mmol) was added to a hexane (5 mL) solution of **1** (0.020 g, 0.051 mmol) under N_2. The suspension was heated at 52 °C for 77 h in an ampule. The solvent was removed, leaving an orange material with some colorless crystals (free ligand) which was taken up in 0.4 mL of hexane and filtered. Removal of the solvent yielded the product in 86% yield (0.022 g). ^{1}H NMR (C_6D_{12}): δ 1.178 (d, J = 8.2 Hz, 9 H), 1.322 (d, J = 2.3 Hz, 15 H), 3.023 (td, J = 7.6, 1.9 Hz, 1 H), 3.664 (td, J = 7.8, 2.4 Hz, 1 H), 3.691 (s, 3 H),

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(29) Jones, W. D.; Feher, F. J. *Inorg. Chem.* **1984**, *23*, 2376–2388.

3.701 (s, 3 H), 6.769 (d, *J* = 2.3 Hz, 1 H), 6.939 (m, 2 H), 6.995 (dd, *J* = 8.8, 2.2 Hz, 1 H). $^{31}P\{^1H\}$ NMR (C_6D_{12}): δ 0.50 (d, *J* = 201.3 Hz).

Preparation of $(C_5Me_5)Rh(PMe_3)(\eta^2$-phenanthrene). $(C_5Me_5)Rh(PMe_3)(Ph)H$ (0.150 g, 0.382 mmol) and 0.700 g of phenanthrene (3.82 mmol) were dissolved in 10 mL of hexane. The mixture was transferred into a glass ampule that was attached to a Teflon stopcock and stirred for 45 h at 64 °C under nitrogen. The reaction mixture was then cooled in an ice–water bath and the solvent removed in vacuo. The orange solid residue, which consisted of free phenanthrene and the desired product, was dissolved in 2 mL of hexane. Cooling (–30 °C) caused the free phenanthrene to crystallize out. The solution was concentrated and cooled again to allow further separation of complex and free ligand. Finally, nice red-orange crystals were obtained in 85% yield. Anal. Calcd for $C_{27}H_{34}PRh$: C, 65.86; H, 6.96. Found: C, 65.53; H, 7.03. ^1H NMR (C_6D_{12}): δ 1.083 (d, *J* = 2.5 Hz, 15 H), 1.151 (d, *J* = 8.2 Hz, 9 H), 3.560 (dd, *J* = 8.0, 2.5 Hz, 2 H), 6.981 (t, *J* = 7.6 Hz, 2 H), 7.118 (t, *J* = 7.4 Hz, 2 H), 7.265 (d, *J* = 8.1 Hz, 2 H), 7.946 (d, *J* = 8.0 Hz, 2 H). $^{31}P\{^1H\}$ NMR (C_6D_{12}): δ 0.31 (d, *J* = 200.9 Hz). $^{13}C\{^1H\}$ NMR (C_6D_{12}): δ 9.58 (s, C_5Me_5), 16.77 (d, *J* = 25.3 Hz, PMe_3), 43.08 (d, *J* = 15.4 Hz, Rh-η^2-CH), 96.43 (t, *J* = 3.6 Hz, C_5Me_5), 122.67 (s, CH), 123.14 (s, CH), 127.00 (s, CH), 129.49 (s, CH), 130.01 (s, C), 143.33 (s, C).

Preparation of $(C_5Me_5)Rh(PMe_3)(1,2\text{-}\eta^2$-anthracene). **1** (0.060 g, 0.153 mmol) was dissolved in 6 mL of hexane. To this solution was added excess anthracene (0.060 g, 0.337 mmol). The suspension was stirred at 67 °C for 137 h. Upon removal of the solvent, the product was then characterized as an η^2-anthracene complex with no hydride being observed by either ^1H or ^{31}P NMR spectroscopy. For $(C_5Me_5)Rh(PMe_3)(1,2\text{-}\eta^2$-anthracene), ^1H NMR (C_6D_6): δ 0.836 (d, *J* = 8.2 Hz, 9 H), 1.318 (d, *J* = 2.4 Hz, 15 H), 3.260 (br m, 1 H), 3.820 (td, *J* = 7.4, 1.9 Hz, 1 H), 6.857 (d, *J* = 4.3 Hz, 2 H), 7.308 (m, 2 H), 7.707 (s, 1 H), 7.854 (d, *J* = 8.0 Hz, 2 H), 7.965 (s, 1 H). $^{31}P\{^1H\}$ NMR: δ 0.59 (d, *J* = 199.6 Hz). $^{13}C\{^1H\}$ NMR: δ 9.68 (s, C_5Me_5), 16.01 (d, *J* = 25.8 Hz, PMe_3), 41.86 (d, *J* =12.8 Hz, Rh-η^2-CH), 42.34 (d, *J* = 13.6 Hz, Rh-η^2-CH), 95.27 (t, *J* = 3.9 Hz, C_5Me_5), 118.23 (s, CH), 124.01 (d, *J* = 7.8 Hz, CH), 124.88 (s, CH), 125.00 (s, CH), 136.21 (s, CH), 131.68 (s, C), 133.01 (s, C), 133.60 (s, C), 141.90 (s, C). Upon standing in THF/hexane at –30 °C for several months, a new complex (5%) was seen which was assigned as a dinuclear complex $[(C_5Me_5)Rh(PMe_3)]_2(1,2\text{-}\eta^2\text{-}3,4\text{-}\eta^2$-anthracene). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 1.80 (d, *J* = 207 Hz). $^{13}C\{^1H\}$ NMR: δ 10.20 (s, C_5Me_5), 16.61 (d, *J* = 24.9 Hz, PMe_3), 96.00 (t, *J* = 3.5 Hz, C_5Me_5). ^1H NMR: δ 0.960 (d, *J* = 8.0 Hz, 18 H), 1.555 (d, *J* = 2.0 Hz, 30 H), 3.442 (m, 2 H), 3.516 (m, 2 H), other expected proton resonances obscured by monomer's proton resonances and C_6D_6.

Reaction of 1 with 2-Methylnaphthalene. A solution of **1** (0.021 g, 0.054 mmol)) and 2-methylnaphthalene (0.090 g, 0.63 mmol) in hexane (5 mL) was heated at 58 °C for 5 days. Following removal of hexane and addition of C_6D_6, a ^{31}P NMR spectrum revealed the presence of three η^2-complexes (δ 1.11 (d, *J* = 204.0 Hz), 62%; 0.77 (d, *J* = 203.3 Hz), 9%; 0.61 (d, *J* = 203.3 Hz), 12%), decomposition complex $(C_5Me_5)Rh(PMe_3)_2$ (δ –6.11 (d, *J* = 217.6 Hz), 9%), and an unknown complex (δ 1.43 (d, *J* = 240.9 Hz), 8%). ^1H and ^1H COSY NMR analysis confirms that the major η^2-product is $(C_5Me_5)Rh(PMe_3)[3,4\text{-}\eta^2$-2-methylnaphthalene]. The other two η^2-complexes were assigned as $(C_5Me_5)Rh(PMe_3)[5,6\text{-}\eta^2$-2-methylnaphthalene] and $(C_5Me_5)Rh(PMe_3)[7,8\text{-}\eta^2$-2-methylnaphthalene], although ^1H NMR data could not be assigned for these two minor products. ^1H NMR ($(C_5Me_5)Rh(PMe_3)[3,4\text{-}\eta^2$-2-methylnaphthalene], C_6D_{12}): δ 1.203 (d, *J* = 8.2 Hz, 9 H), 1.261 (s, 15 H), 2.055 (s, 3 H), 3.086 (td, *J* = 7.3, 2.8 Hz, 1 H), 3.756 (td, *J* = 7.4, 2.8 Hz, 1 H), 6.340 (s, 1 H), 6.857 (t, *J* = 7.4 Hz, 1 H), 6.986 (t, *J* = 7.4 Hz, 1 H), 7.043 (d, *J* = 7.7 Hz, 1 H), 7.242 (d, *J* = 7.5 Hz, 1 H).

Reaction of 1 with Styrene. Styrene (0.04 mL, 0.35 mmol) was added to a hexane solution of **1** (0.020 g, 0.051 mmol) (pale-green color) in an ampule under N_2. The solution became orange immediately. The reaction mixture was stirred for 20 h at 60 °C. Upon removal of the solvent, the orange material was analyzed by NMR spectroscopy. Two η^2-olefin complexes were formed on the basis of ^1H and ^{31}P NMR data which were assigned as two rotamers of $(C_5Me_5)Rh(PMe_3)(\eta^2$-styrene). $^{31}P\{^1H\}$ NMR (C_6D_6): $(C_5Me_5)Rh(PMe_3)(\eta^2$-styrene) (rotamer A), δ –0.90 (d, *J* = 193.5 Hz), 72%; $(C_5Me_5)Rh(PMe_3)(\eta^2$-styrene) (rotamer B), δ –6.54 (d, *J* = 202.7 Hz), 28%. ^1H NMR: (rotamer A) δ 0.908 (dd, *J* = 8.3, 1.1 Hz, 9 H), 1.624 (d, *J* = 2.4 Hz, 15 H), 1.721 (m, 1 H), 2.193 (qd, 1 H), 3.466 (qd, *J* = 7.5, 2.6 Hz, 1 H), 7.014 (t, 1 H), 7.075 (t, 1 H), 7.25 (m, 2 H), 7.439 (d, *J* = 8.0 Hz, 1 H). (rotamer B) δ 0.693 (dd, *J* = 8.8, 1.0 Hz, 9 H), 1.867 (d, *J* = 1.8 Hz, 15 H), 2.231 (m, 1 H, 3.812 (td, *J* = 8.1, 2.8 Hz, 1 H), 6.997 (d, *J* = 8.0 Hz, 1 H), 7.614 (d, *J* = 8.0 Hz, 1 H). Other proton resonances were obscured by rotamer A.

Reaction of 1 with Fluoranthene. Fluoranthene (0.026 g, 0.13 mmol) was added to a hexane solution of **1** (0.015 g, 0.038 mmol) under N_2 and the solution heated at 65 °C for 47 h. Upon removal of the solvent, the brown material was examined by NMR spectroscopy. The ^{31}P NMR showed a single resonance (δ –0.02 (d, *J* = 199.0 Hz)) which revealed that only one η^2-complex was produced. The ^1H COSY NMR was consistent with the formulation of $(C_5Me_5)Rh(PMe_3)(\eta^2$-fluoranthene). ^1H NMR (C_6D_6): δ 0.800 (dd, *J* = 8.3 Hz, 9 H), 1.220 (d, *J* = 1.6 Hz, 15 H), 3.480 (qd, *J* = 6.3, 2.6 Hz, 1 H), 3.679 (td, *J* = 7.4, 2.6 Hz, 1 H), 7.260 (d, *J* = 6.5 Hz, 1 H), 7.280 (d, *J* = 5.6 Hz, 1 H), 7.480 (d, *J* = 7.5 Hz, 1 H), 7.58 (br d, 1 H), 7.654 (m, 2 H), 7.830 (m, 2 H).

Preparation of $(C_5Me_5)Rh(PMe_3)(\eta^2$-pyrene). Pyrene (0.045 g, 0.22 mmol) was added to a solution of **1** (0.020 g, 0.051 mmol) in hexane (4 mL). After the reaction mixture was heated at 60 °C for 21 h, the solvent was removed in vacuo (25 °C, 10^{-4} mmHg). A ^{31}P NMR spectrum (C_6D_{12}) revealed the presence of two Rh(I) complexes. The major doublet resonance was attributable to the η^2-complex $(C_5Me_5)Rh(PMe_3)(4,5\text{-}\eta^2$-pyrene) ($\delta$ 0.20 (d, *J* = 200.5 Hz), 90%), and the minor product was assigned as the dinuclear complex $[(C_5Me_5)Rh(PMe_3)]_2(4,5\text{-}\eta^2\text{-}9,10\text{-}\eta^2$-pyrene) ($\delta$ 0.11 (d, *J* = 202.9 Hz), 10%). The assignment of the major product as the 4,5-isomer was based on ^1H NMR data. ^1H NMR (C_6D_{12}): δ 0.767 (s, 15 H), 1.163 (d, *J* = 7.8 Hz, 9 H), 3.827 (dd, *J* = 7.9, 1.8 Hz, 2 H), 7.565 (s, 2 H), 7.800 (t, *J* = 7.5 Hz, 4 H), 8.008 (d, *J* = 7.6 Hz, 2 H).

Reaction of 1 with Perylene. Perylene (220 mg, 0.87 mmol) was added to a THF solution of **1** (106 mg, 0.27 mmol, in 10 mL) and heated at 58 °C for 3 weeks. The solvent was removed under vacuum and the residue extracted with 5 mL of hexane. The solution was filtered and cooled to –30 °C, and the black-green crystals that formed were isolated by filtration. Yield: 54 mg (13%). For $(C_5Me_5)Rh(PMe_3)(\eta^2$-perylene), ^1H NMR (THF-d_8): δ 1.30 (dd, *J* = 8.5, 0.8 Hz, 9 H), 1.35 (d, *J* = 2.6 Hz, 15 H), 3.61 (qd, *J* = 6.4, 2.3 Hz, 1 H), 3.75 (td, *J* = 7.3, 2.6 Hz, 1 H), 7.23 (t, *J* = 7.6 Hz, 1 H), 7.31 (m, 3 H), 7.49 (d, *J* = 7.9 Hz, 1 H), 7.52 (d, *J* = 7.6 Hz, 1 H), 7.83 (dd, *J* = 7.9, 1.2 Hz, 1 H), 7.87 (d, *J* = 6.4 Hz, 1 H), 8.01 (d, *J* = 6.7 Hz, 2 H). $^{13}C\{^1H\}$ NMR (JMOD, THF-d_8): δ 10.3 (s, $C_5\mathit{Me}_5$), 16.4 (d, *J* = 25.7 Hz, PMe_3), 45.1 (dd, *J* = 14.3, 1.9 Hz, η^2-CH), 45.5 (d, *J* = 12.4 Hz, η^2-CH), 96.7 (dd, *J* = 4.8, 2.4 Hz, C_5Me_5), 117.1 (s, CH), 117.9 (s, CH), 118.9 (s, CH), 121.8 (s, C), 125.2 (s, CH), 126.8 (s, CH), 126.9 (s, CH), 127.0 (s, CH), 127.2 (s, CH), 128.1 (s, C), 128.4 (s, CH), 129.4 (s, C), 130.1 (s, C), 133.6 (s, C), 134.3 (s, C), 134.8 (s, CH), 136.5 (s, C), 143.5 (s, C). $^{31}P\{^1H\}$ NMR (C_6D_{12}): δ 0.79 (d, *J* = 198 Hz). For $(C_5Me_5)Rh(PMe_3)(C_{20}H_{11})H$, ^1H NMR (THF-d_8): δ –13.53 (dd, *J* = 48, 31 Hz, 1 H), 1.27 (dd, *J* = 10, 1.2 Hz, 9 H), 1.89 (dd, *J* = 2.3, 1.2 Hz, 15 H), 7.34 (m, 2 H), 7.51 (m, 2 H), 7.68 (m, 1 H), 7.97 (d, *J* = 7.3 Hz, 1 H), 8.12 (t, *J* = 7.3 Hz, 2 H), 8.26 (d, *J* = 7.6 Hz, 1 H), 8.40 (br s, 1 H). $^{13}C\{^1H\}$ NMR (JMOD, THF-d_8): δ 10.9 (s, $C_5\mathit{Me}_5$), 19.3 (d, *J* = 31.5 Hz, PMe_3), 98.3 (t, *J* = 3.3 Hz, C_5Me_5), 118.1 (s, CH), 119.4 (s, CH), 120.1 (s, CH), 121.1 (s, CH), 125.9 (s, CH), 127.3 (s, CH), 127.5 (s, C), 127.7 (s, CH), 128.6 (s, CH), 130.3 (s, C), 131.7 (s, C), 132.2 (s, C), 133.1 (s, C), 133.8 (s, C), 135.7 (s, C), 136.2 (s, C). $^{31}P\{^1H\}$ NMR (C_6D_{12}): δ 8.31 (d, *J* = 152 Hz).

X-ray Structural Determination of $(C_5Me_5)Rh(PMe_3)[2,3\text{-}\eta^2$-perylene]. A small red crystal of the complex was mounted on a glass fiber with epoxy and placed in the cold stream (–20 °C) of the diffractometer. Twenty-five reflections with values of χ between 5° and 70° were centered and used for cell determination. Data were collected in a *C*-centered monoclinic crystal system, and data reduction showed absences consistent with space group *C*2/*c*. Solution of the Patterson map allowed placement of the rhodium atom, and use of the program DIRDIF allowed location of all remaining atoms. A THF solvent molecule was found in a crystal void located on a 2-fold axis. It was also noticed following isotropic refinement that the PMe_3 was rotationally disordered, and isotropic refinement of the two rotamer populations was carried out (68.6/31.4). An absorption correction was applied with the program DIFABS. In the final model, hydrogens were placed in idealized positions and all non–hydrogen atoms were refined anisotropically with the exception of the disordered PMe_3 carbons, the THF molecule, and C20, which were left isotropic. (Anisotropic refinement of C20 led to a nonpositive definite thermal parameter.) Data collection and refinement parameters are given in Table VI.

Reaction of 1 with Triphenylene. **1** (15 mg, 0.038 mmol) was reacted with a 5-fold excess of triphenylene in 0.5 mL of cyclohexane-d_{12} at 60 °C for 48 h. A ^{31}P NMR spectrum showed the presence of a major new product (60%) at δ 2.039 (d, *J* = 209 Hz), plus a smaller amount (40%) of a C–H activation product (δ 7.66 (d, *J* = 152 Hz)). The ^1H NMR

Table VI. Crystallographic Data for $(C_5Me_5)Rh(PMe_3)(2,3\text{-}\eta^2\text{-perylene})$

crystal parameters	
chemical formula	$RhPC_{35}H_{40}O_{0.5}$
formula weight	602.58
space group (no.)	$C2/c$ (#15)
Z	8
a, Å	32.927(10)
b, Å	10.125(2)
c, Å	18.129(8)
β, deg	100.30(3)
Vol, Å^3	5946(6)
ρ_{calcd}, g cm^{-3}	1.35
cryst dimens, mm	0.08 × 0.11 × 0.22
temp, °C	−20
radiation (monochromatic)	Mo, 0.710 73 Å (graphite)
scan type	$2\theta/\omega$
2θ range, deg	4–44
no. of data collected	3992
no. of unique data $F^2 > 3\sigma(F^2)$	1703
no. of params varied	318
μ, cm^{-1}	6.40
$R(F_o)$	0.0532
$R_w(F_o)$	0.0518
goodness of fit	1.35

spectrum also showed evidence for a bis-η^2-complex. For $[(C_5Me_5)Rh(PMe_3)]_2(1,2\text{-}\eta^2\text{-}3,4\text{-}\eta^2\text{-triphenylene})$, ^{1}H NMR ($C_6D_{12}$): δ 1.325 (d, J = 8.2 Hz, 18 H), 1.233 (d, J = 2.4 Hz, 30 H), 3.464 (m, 4 H), 8.43 (d, J = 7.4 Hz, 2 H), other aromatic resonances obscured by excess triphenylene. For $(C_5Me_5)Rh(PMe_3)$(2-triphenylenyl)H, ^{1}H NMR (C_6D_{12}): δ −13.40 (dd, J = 49, 30 Hz, 1 H), 1.187 (dd, J = 10.2, 1.2 Hz, 9 H), 1.866 (s, 15 H), 8.023 (d, J = 8.2 Hz, 1 H), other aromatic resonances obscured by free triphenylene. Heating for an additional 24 h resulted in no change.

Temperature-Dependent Equilibria between the Rh(I) η^2-Arene Complex and Rh(III) Aryl Hydride. **1** (0.040 g, 0.102 mmol) reacted with excess naphthalene (10-fold excess) in hexane at 60 °C to give a 2:1 mixture of $(C_5Me_5)Rh(PMe_3)(\eta^2\text{-naphthalene})$ and $(C_5Me_5)Rh(PMe_3)$(2-naphthyl)H. The solvent was removed in vacuo, and the solid product was dissolved in 0.6 mL of C_6D_{12}. The solution was placed into a resealable NMR tube. The sample was heated in an oil bath with controlled temperature, and ^{31}P NMR spectra were recorded periodically until the compound ratios did not change. The equilibration of the η^2-naphthalene complex and the naphthyl hydride was measured over a 50 °C temperature range. The parameters of $\Delta H°$ = −4.13(0.02) kcal/mol and $\Delta S°$ = −12.0–(0.1) cal/(mol K) were calculated from a Van't Hoff plot (Figure 1).

Reaction of $(C_5H_5)Rh(PMe_3)(Ph)H$ with Naphthalene. A solution of $(C_5H_5)Rh(PMe_3)(Ph)H$ and excess naphthalene in cyclohexane-d_{14} was heated to 40 °C for several hours. Changes in the ^{1}H, ^{31}P, and ^{13}C NMR spectra were consistent with the disappearance of the phenylhydride complex and the appearance of the η^2-naphthalene complex. For $(C_5H_5)Rh(PMe_3)(\eta^2\text{-naphthalene})$, ^{1}H NMR ($C_7D_{14}$): δ 1.29 (dd, J = 9.3, 0.9 Hz, 9 H), 3.49 (qd, J = 5.6, 2.4 Hz, 1 H), 4.09 (td, J = 6.6, 2.6 Hz, 1 H), 4.35 (d, J = 0.7 Hz, 5 H), 6.42 (d, J = 8.8 Hz, 1 H), 7.05 (td, J = 7.6, 1.6 Hz, 1 H), 7.17 (m, 3 H), 7.63 (d, J = 7.6 Hz, 1 H). ^{13}C{^{1}H} NMR: δ 20.09 (dd, J = 24.7, 1.4 Hz, PMe_3), 47.52 (dd, J = 14.1, 1.8 Hz, C_{coord}), 49.11 (dd, J = 14.1, 1.8 Hz, C_{coord}), 88.59 (t, J = 3.3 Hz, C_5H_5), 119.59 (s, C), 123.61 (s, C), 126.68 (s, C), 127.87 (s, C), 128.45 (s, C), 137.52 (s, C). ^{31}P{^{1}H} NMR: δ 3.76 (d, J = 200 Hz). Continued heating of the sample resulted in a decrease in the intensity of the above resonances and an increase of resonances attributable to the binuclear adduct. For $[(C_5H_5)Rh(PMe_3)]_2(1,2\text{-}\eta^2\text{-}3,4\text{-}\eta^2\text{-naphthalene})$, ^{1}H NMR ($C_7D_{14}$): δ 1.29 (dd, J = 9.3, 0.9 Hz, 9 H), 3.31 (td, J = 5.8, 2.1 Hz, 1 H), 3.91 (m, 1 H), 4.55 (d, J = 0.6 Hz, 5 H), 6.85 (dd, J = 5.7, 3.3 Hz, 1 H), 7.20 (dd, J = 5.7, 3.3 Hz, 1 H). ^{31}P{^{1}H} NMR: δ 5.05 (d, J = 208 Hz).

Reaction of $(C_5H_5)Rh(PMe_3)(C_2H_4)$ with $1,4\text{-}C_6H_4(CF_3)_2$. A solution of $(C_5H_5)Rh(PMe_3)(C_2H_4)$ in neat 1,4-bis(trifluoromethyl)benzene (0.055 M) was irradiated (λ > 285 nm) for 18 h. A ^{1}H NMR spectrum was recorded, showing a 67% conversion of starting material and two new species in a 4.4:1 ratio, identified as $(C_5H_5)Rh(PMe_3)[\eta^2\text{-}C_6H_4(CF_3)_2]$ and $(C_5H_5)Rh(PMe_3)[2,5\text{-}C_6H_3(CF_3)_2]H$, respectively, on the basis of their ^{1}H and ^{31}P NMR spectra. For $(C_5H_5)Rh(PMe_3)[\eta^2\text{-}C_6H_4(CF_3)_2]$, ^{1}H NMR ($C_6D_6$): δ 0.59 (dd, J = 9.3, 1.0 Hz, 9 H), 3.34 (dd, J = 5.6, 2.7 Hz, 2 H), 4.45 (t, J = 0.8 Hz, 5 H), 6.26 (s, 2 H). ^{13}C{^{1}H} NMR (C_6D_6): δ 18.58 (d, J = 28.1 Hz, PMe_3), 43.30 (d, J = 13.5 Hz, CH_{coord}), 89.31 (dd, J = 3.8, 2.9 Hz, C_5H_5). ^{19}F NMR (C_6D_6): δ −64.82 (s). ^{31}P{^{1}H} NMR (C_6D_6): δ 1.26 (d, J = 188.3 Hz). For $(C_5H_5)Rh(PMe_3)\text{-}[2,5\text{-}C_6H_3(CF_3)_2]H$, ^{1}H NMR ($C_6D_6$): δ −13.22 (dd, J = 45.5, 26.3 Hz, 1 H), 0.72 (dd, J = 10.5, 1.6 Hz, 9 H), 4.99 (d, J = 1.4 Hz, 5 H), 7.06 (d, J = 8.2 Hz, 1 H), 7.52 (d, J = 8.2 Hz, 1 H), 8.18 (s, 1 H). ^{13}C{^{1}H} NMR (C_6D_6): δ 21.36 (d, J = 33.0 Hz, PMe_3), 88.25 (t, J = 2.0 Hz, C_5H_5). ^{19}F NMR (C_6D_6): δ −62.38 (s, 3 F), −58.67 (br s, 3 F). ^{31}P{^{1}H} NMR (C_6D_6): δ 12.24 (d, J = 152.0 Hz).

Reaction of $(C_5H_5)Rh(PMe_3)(C_2H_4)$ with $1,3\text{-}C_6H_4(CF_3)_2$. A solution of $(C_5H_5)Rh(PMe_3)(C_2H_4)$ in 1,3-bis(trifluoromethyl)benzene (0.03 M) was irradiated (λ > 285 nm) for 40 h. A ^{31}P NMR spectrum showed conversion to a Rh(III) product (95.4%) plus a Rh(I) product (4.6%). For $(C_5H_5)Rh(PMe_3)[3,5\text{-}C_6H_3(CF_3)_2]H$, ^{1}H NMR (toluene-$d_8$): δ −13.65 (dd, J = 41.8, 30.5 Hz, 1 H), 0.77 (dd, J = 10.6, 1.2 Hz, 9 H), 4.88 (d, J = 1 Hz, 5 H), 7.56 (s, 1 H), 8.08 (s, 2 H). ^{19}F NMR (toluene-d_8): δ −62.31 (s). ^{31}P{^{1}H} NMR (toluene-d_8): δ 13.83 (d, J = 151 Hz). For $(C_5H_5)Rh(PMe_3)[4,5\text{-}\eta^2\text{-}1,3\text{-}C_6H_4(CF_3)_2]$, ^{1}H NMR (toluene-$d_8$): δ 0.70 (dd, J = 9.3, 1.0 Hz, 9 H), 3.07 (m, 1 H), 4.48 (t, J = 0.8 Hz, 5 H), 6.73 (s, 1 H), 7.63 (d, J = 8.1 Hz, 1 H). (The second coordinated arene proton is obscured.) ^{19}F NMR (toluene-d_8): −63.09 (s), −62.20 (s). ^{31}P{^{1}H} NMR (toluene-d_8): δ 2.99 (d, J = 188 Hz).

Reaction of $(C_5Me_5)Rh(PMe_3)(Ph)H$ with $1,4\text{-}C_6H_4(CF_3)_2$. A solution of $(C_5Me_5)Rh(PMe_3)(Ph)H$ (35 mg, 0.089 mmol) and 1,4-bis(trifluoromethyl)benzene (38 mg, 0.18 mmol) in 0.5 mL of cyclohexane-d_{12} was heated for 20 h. ^{1}H NMR spectra were recorded at regular intervals and showed conversion of starting material to a single new metal hydride product. For $(C_5Me_5)Rh(PMe_3)[2,5\text{-}C_6H_3(CF_3)_2]H$, ^{1}H NMR ($C_6D_6$): δ −12.91 (dd, J = 51.4, 28.5 Hz, 1 H), 0.70 (dd, J = 9.9, 1.1 Hz, 9 H), 1.60 (dd, J = 2.3, 0.9 Hz, 15 H), 7.07 (d, J = 8.5 Hz, 1 H), 7.55 (d, J = 8.2 Hz, 1 H), 8.06 (s, 1 H). ^{13}C{^{1}H} NMR (C_6D_6): δ 10.27 (s, C_5*Me*$_5$), 18.13 (dd, J = 32.6, 1.4 Hz, PMe_3), 98.19 (t, J = 3.3 Hz, C_5Me_5), 118.34 (q, J = 4.1 Hz, C_{para}), 126.16 (dt, J = 6.3, 1.7 Hz, C_{meta}), 140.28 (m, C_{ortho}), 142.28 (t, J = 3.0 Hz, C_{ipso}). ^{19}F NMR (C_6D_6): δ −62.44 (s, 3 F), −59.52 (s, 3 F). ^{31}P{^{1}H} NMR (C_6D_6): δ 6.23 (d, J = 146.7 Hz).

Reaction of $(C_5H_5)Ir(PMe_3)H_2$ with $1,4\text{-}C_6H_4(CF_3)_2$. A solution of $(C_5H_5)Ir(PMe_3)H_2$ in 1,4-bis(trifluoromethyl)benzene (0.015 M) was irradiated (λ > 285 nm) for 2 h. A ^{1}H NMR spectrum showed 50% conversion to a single metal hydride product. For $(C_5H_5)Ir(PMe_3)[2,5\text{-}C_6H_3(CF_3)_2]H$, ^{1}H NMR ($C_6D_6$): δ −16.55 (d, J = 35.8 Hz, 1 H), 0.91 (d, J = 10.6 Hz, 9 H), 4.72 (s, 5 H), 7.07 (d, J = 8.0 Hz, 1 H), 7.54 (d, J = 8.3 Hz, 1 H), 8.32 (s, 1 H). ^{19}F NMR (C_6D_6): δ −62.38 (s, 3 F), −58.15 (s, 3 F). ^{31}P{^{1}H} NMR (C_6D_6): δ −37.83 (s).

Reaction of $(C_5H_5)Rh[P(OMe)_3](C_2H_4)$ with $1,4\text{-}C_6H_4(CF_3)_2$. A solution of $(C_5H_5)Rh[P(OMe)_3](C_2H_4)$ in 1,4-bis(trifluoromethyl)benzene (~0.02 M) was irradiated (λ > 285 nm) for 14 h. ^{1}H, ^{13}C(DEPT), and ^{31}P NMR spectra were recorded, showing 60% conversion to two new products with assignments as described in the text. For $(C_5H_5)Rh[P(OMe)_3][\eta^2\text{-}C_6H_4(CF_3)_2]$, ^{1}H NMR ($C_6D_6$): δ 3.20 (d, J = 12.6 Hz, 9 H), 4.09 (t, J = 3.1 Hz, 2 H), 4.53 (dd, J = 2.0, 0.7 Hz, 5 H), 6.28 (s, 2H). ^{13}C{^{1}H} NMR (C_6D_6): δ 47.51 (d, J = 11.9 Hz, C_{coord}), 50.73 (s, OMe), 90.17 (t, J = 3.9 Hz, C_5H_5). ^{19}F NMR (C_6D_6): δ −64.77 (s). ^{31}P{^{1}H} NMR (C_6D_6): δ 149.2 (d, J = 290.5 Hz). For $(C_5H_5)Rh[P(O)(OMe)_2](C_2H_4)Me$, ^{1}H NMR ($C_6D_6$): δ 1.16 (t, J = 2.0 Hz, 3 H), 2.77 (m, 2 H), 3.39 (m, 2 H), 3.63 (d, J = 11.0 Hz, 3 H), 3.65 (d, J = 11.0 Hz, 3 H), 4.81 (dd, J = 2.4, 0.4 Hz, 5 H). ^{13}C{^{1}H} NMR (C_6D_6): δ −12.75 (dd, J = 21.9, 10.5 Hz, RhMe), 51.51 (d, J = 9.2 Hz, OMe), 51.92 (d, J = 9.2 Hz, OMe), 52.57 (dd, J = 9.3, 2.8 Hz, C_2H_4), 93.22 (t, J = 3.0 Hz, C_5H_5). ^{31}P{^{1}H} NMR (C_6D_6): δ 77.13 (d, J = 166.0 Hz).

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Supplementary Material Available: Tables of bond distances, angles, fractional atomic coordinates, anisotropic thermal parameters, and least squares planes (10 pages); table of calculated and observed structure factors for the complexes $(C_5Me_5)Rh(PMe_3)(2,3\text{-}\eta^2\text{-perylene})$ (13 pages). Ordering information is given on any current masthead page.