Control of η²-Arene Coordination and C–H Bond Activation by Cyclopentadienyl Complexes of Rhodium

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The selectivity for C–H bond activation vs. η²-coordination of arenes with [(η⁵-C₅R₅)Rh(PMe₃)] fragments (R = Me, H) is subject to control by the thermodynamic stability of the resulting η²-arene complex; the preference for η²-coordination increases in order of arene: benzene < 1,4-C₆H₄(CF₃)₂ < naphthalene, and in order of ancillary ligand: C₅Me₅ < C₅H₅.

It was proposed many years ago that arene insertion reactions were preceded by η²-arene coordination.[1,2] Recently, we have found experimental evidence for such a mechanism in the reactions of η⁵-C₅H₅ and η⁵-C₅Me₅ rhodium complexes and have controlled the preference for η²-arene vs. (aryl)hydride complexation by using fused polycyclic aromatic systems.[3–5] Here, we quantify the thermodynamics and kinetics of these reactions and show how the outcome can be controlled further by substitution of the cyclopentadienyl ring.

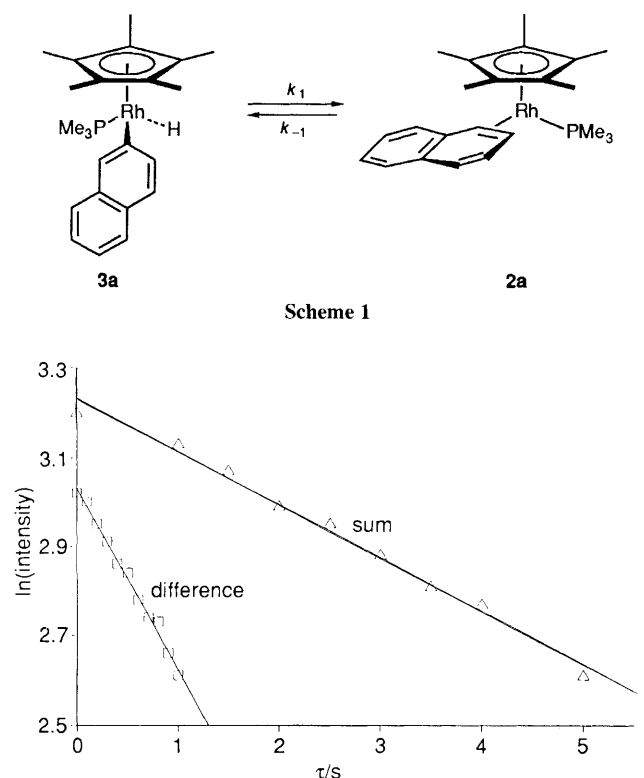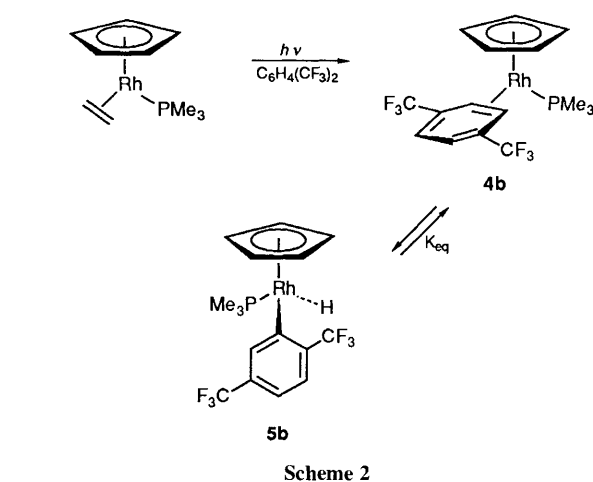The thermal reaction (60 °C) of [(C₅Me₅)Rh(PMe₃)(Ph)H]

Scheme 1

Fig. 1 First-order plots of the time dependence of ln $(I_{2a} + I_{3a})$ (sum) and ln $(I_{2a} - I_{3a})$ (difference) for the intensities of the ^{31}P resonances of **2a** and **3a** observed in the spin saturation transfer experiment at 312 K. A selective 180° pulse inverts the resonance of **3a** and is followed by a non-selective 90° pulse after a time τ. The slope of the sum line corresponds to $-1/T_1$ while the difference line has a slope $-(1/T_1 + 2k_1)$, where k_1 is the rate of exchange in Scheme 1 and T_1 is the mean relaxation time.

Scheme 2

The corresponding C_5H_5 complex $[(C_5H_5)Rh(PMe_3)(\eta^2$-naphthalene)] **2b** can also be prepared by thermolysis (40 °C) of $[(C_5H_5)Rh(PMe_3)(Ph)H]$ **1b** in the presence of naphthalene.‡ In this case none of the C–H activation adduct **3b** is observed. The lesser electron donating ability of the C_5H_5 ligand manifests itself as a stabilisation of the Rh^I species.[7]

This electronic effect is also found in examination of reactions with hexafluoro-p-xylene. Irradiation of a solution of $[(C_5H_5)Rh(PMe_3)(C_2H_4)]$ in 1,4-$C_6H_4(CF_3)_2$ results in efficient loss of ethene, giving an equilibrium mixture of $[(C_5H_5)Rh(PMe_3)\{\eta^2$-$C_6H_4(CF_3)_2\}]$ **4b** and $[(C_5H_5)Rh-(PMe_3)\{C_6H_3(CF_3)_2\}H]$ **5b** (Scheme 2).‡ The equilibrium varies slightly and reproducibly with changes in solvent,§ and

1a with an excess of naphthalene produces a 2:1 mixture of $[(C_5Me_5)Rh(PMe_3)(\eta^2$-naphthalene)] **2a** and $[(C_5Me_5)$-Rh(PMe_3)(2-naphthyl)H] **3a**.[4] We have now demonstrated that these species are in equilibrium (Scheme 1) by magnetization transfer between the phosphorus nuclei in the ^{31}P NMR spectrum.† The rate of spin saturation transfer from $[(C_5Me_5)Rh(PMe_3)(2$-naphthyl)H] **3a** to $[(C_5Me_5)Rh(PMe_3)$-$(\eta^2$-naphthalene)] **2a** in $[^2H_{12}]$cyclohexane was quantitatively determined by selective inversion of the resonance for the former followed by a nonselective 90° pulse after a variable (0–10 s) delay. Plots of the sum and difference of the intensities of the resonances for the two complexes give lines whose slopes correspond to $-1/T_1$ and $-(1/T_1 + 2k_1)$, as shown in Fig. 1.[6] The rate of this interconversion was determined over a range of 25 °C, giving activation parameters of $\Delta H^{\ddagger} = 70.6 \pm 3.3$ kJ mol^{-1} and $\Delta S^{\ddagger} = -35 \pm 12$ J mol^{-1} K^{-1}.

Equilibration of these two complexes with benzene by heating **1a** in a 1.12:1 mixture of naphthalene and benzene in $[^2H_{12}]$cyclohexane solution at 50 °C leads to the formation of a 1.31:0.80:1.0 equilibrium mixture of **2a**:**3a**:**1a**. These ratios correspond to free energy differences of 1.3 kJ mol^{-1} favouring the η^2-complex over the naphthyl hydride, and 0.9 kJ mol^{-1} favouring the phenyl hydride over the naphthyl hydride. If the mixture of **2a** and **3a** is heated in benzene solution (51 °C), the rate of naphthalene loss can be measured from the rate of disappearance of **3a** ($k = 1.1 \times 10^{-5}$ s^{-1}).

‡ Spectral data: NMR at 300 MHz for ^1H in C_6D_6; ^1H spectra relative to C_6D_5H at δ 7.13, or C_7D_{14} at δ 1.63, ^{13}C spectra relative to C_6D_6 at δ 128.0 or C_7D_{14} at δ 21.9, ^{31}P spectra relative to external H_3PO_4, ^{19}F spectra relative to external $CFCl_3$; coupling constants in Hz.

$[(C_5H_5)Rh(PMe_3)(\eta^2$-naphthalene)] **2b**, ^1H (C_7D_{14}): δ 7.63 (d, 1H, J 7.6, H^8 or H^5), 7.17 (m, 3H, H^3, H^5 or H^8, H^7 or H^6), 7.05 (td, 1H, J 7.6, 1.2, H^6 or H^7), 6.42 (d, 1H, J 8.8, H^4), 4.35 (d, 5H, J_{PH} 0.7, C_5H_5), 4.09 (td, 1H, J 6.6, 2.6, H^1), 3.49 (qd, 1H, J 5.6, 2.4, H^2) and 1.29 (dd, 9H, J_{PH} 9.3, J_{RhH} 0.9, PMe$_3$), assignments by COSY (500 MHz); ^{31}P (C_7D_{14}): δ 3.76 (d, J_{RhP} 199.5); ^{13}C (C_7D_{14}): δ 137.52 (s), 128.45 (s), 127.87 (s), 126.68 (s), 123.61 (s), 119.59 (s), 88.59 (t, J_{PC} = J_{RhC} = 3.3, C_5H_5), 49.11 (dd, J_{PC} 14.1, J_{RhC} 1.8, η^2-C), 47.52 (dd, J_{PC} 14.1, J_{RhC} 1.8, η^2-C), 20.09 (dd, J_{PC} 24.7, J_{RhC} 1.4, PMe$_3$).

$[(C_5H_5)Rh(PMe_3)\{\eta^2$-$C_6H_4(CF_3)_2\}]$ **4b**, ^1H (C_6D_6): δ 6.26 (s, 2H, C_6H_4 uncoordinated C–H), 4.45 (t, 5H, J_{PH} = J_{RhH} = 0.8, C_5H_5), 3.34 (dd, 2H, J_{PH} 5.6, J_{RhH} 2.7, C_6H_4 coordinated C–H) and 0.59 (dd, 9H, J_{PH} 9.3, J_{RhH} 1.0, PMe$_3$); ^{31}P (C_6D_6): δ 1.26 (d, J_{RhP} 188.3, PMe$_3$); ^{19}F (C_6D_6): δ -64.82 (s, CF$_3$); ^{13}C (C_6D_6): δ 89.31 (dd, J_{PC} 3.8, J_{RhC} 2.9, C_5H_5), 43.30 (d, J_{PC} 13.5, C_6H_4, coordinated carbon) and 18.58 (d, J_{PC} 28.1, PMe$_3$).

$[(C_5Me_5)Rh(PMe_3)\{2,5-C_6H_3(CF_3)_2\}H]$ **5a**, ^1H (C_6D_6): δ 8.06 (s, 1H, H^6), 7.55 (d, 1H, J_{HH} 8.2, H^3 or H^4), 7.07 (d, 1H, J_{HH} 8.5, H^4 or H^3), 1.60 (dd, 15H, J_{PH} 2.3, J_{RhH} 0.9, C_5Me_5), 0.70 (dd, 9H, J_{PH} 9.9, J_{RhH} 1.1, PMe$_3$) and -12.91 (dd, 1H, J_{PH} 51.4, J_{RhH} 28.5, RhH); ^{31}P (C_6D_6): δ 6.23 (d, J_{RhP} 146.7); ^{19}F (C_6D_6): δ -59.52 (s, CF$_3$) and -62.44 (s, CF$_3$); ^{13}C (C_6D_6): δ 142.28 (t, J_{PC} = J_{RhC} = 3.0, C^1), 140.28 (m, C^6), 126.16 (dt, J 6.3, 1.7, C^3), 118.34 (q, J 4.1, C^4), 98.19 (t, J_{PC} = J_{RhC} = 3.3, C_5Me_5), 18.13 (dd, J_{PC} 32.6, J_{RhC} 1.4, PMe$_3$) and 10.27 (s, C_5Me_5).

$[(C_5H_5)Rh(PMe_3)\{2,5-C_6H_3(CF_3)_2\}H]$ **5b**, ^1H (C_6D_6): δ 8.18 (s, 1H, H^6), 7.52 (d, 1H, J_{HH} 8.2, H^3), 7.06 (d, 1H, J_{HH} 8.2, H^4), 4.99 (d, 5H, J_{PH} 1.4, C_5H_5), 0.72 (dd, 9H, J_{PH} 10.5, J_{RhH} 1.6, PMe$_3$) and -13.22 (dd, 1H, J_{PH} 45.5, J_{RhH} 26.3, RhH); ^{31}P (C_6D_6): δ 12.24 (d, J_{RhP} 152, PMe$_3$); ^{19}F (C_6D_6): δ -58.67 (br. s, CF$_3$) and -62.38 (s, CF$_3$); ^{13}C (C_6D_6): δ 88.25 (t, J_{PC} = J_{RhC} = 2.0, C_5H_5) and 21.36 (d, J_{PC} 33, PMe$_3$).

§ K_{eq} expressed as [**4b**]/[**5b**] varies from 4.4 in C_6D_6 to 2.9 in CD_3CN solution and is temperature independent between -30 and $+50$ °C, implying that ΔH is small.
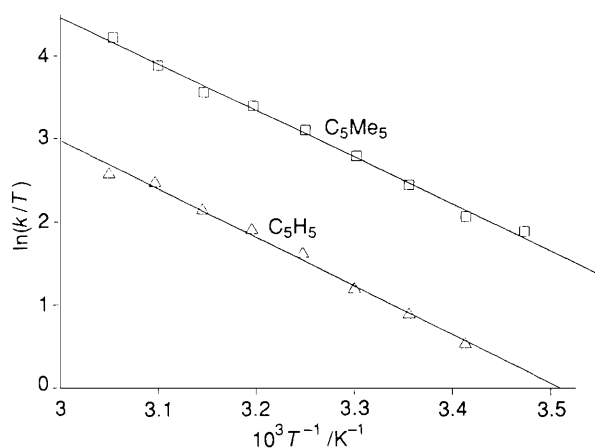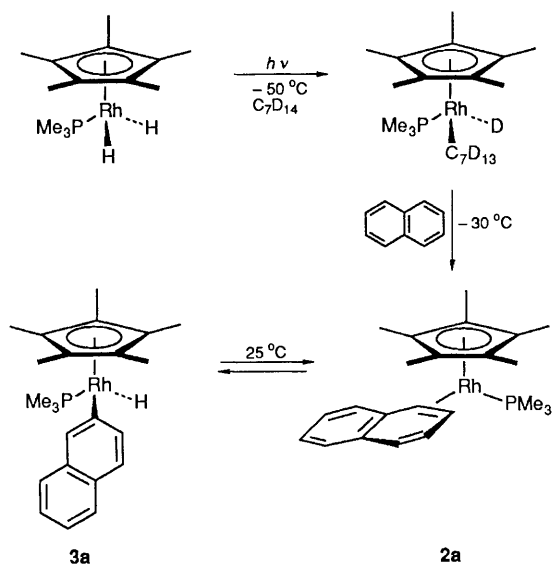
Scheme 3

Fig. 2 Eyring plots of the temperature dependence of the rate constants for the decay of the transients observed on laser flash photolysis of $[(C_5H_5)Rh(PMe_3)(C_2H_4)]$ ($\triangle$) and $[(C_5Me_5)Rh(PMe_3)(C_2H_4)]$ ($\square$) in benzene. The transients are assigned to the complexes $[(\eta^5\text{-}C_5R_5)Rh(PMe_3)(\eta^2\text{-}C_6H_6)]$, which decay to form $[(\eta^5\text{-}C_5R_5)Rh(PMe_3)(C_6H_5)H]$. The activation parameters are given in the text. The data for $[(C_5H_5)Rh(PMe_3)(C_2H_4)]$ are taken from ref. 5.

magnetisation transfer is seen between the C_5H_5 resonances for the two complexes at 60 °C. For comparison, the C_5Me_5 analogues were prepared either by irradiation of $[(C_5Me_5)Rh(PMe_3)(C_2H_4)]$ or by thermolysis of **1a** in the presence of the fluorinated arene. Only the C–H activation product **5a** is seen with the C_5Me_5 ligand,‡ however, again indicating that the equilibrium between η^2-arene and aryl hydride can be controlled by choice of the ring substituents.

The question of intermediacy of η^2-arene coordination to $(C_5Me_5)Rh(PMe_3)$ *prior* to C–H bond oxidative addition can also be examined both in the reaction with naphthalene and with benzene. For naphthalene, η^2-arene coordination was observed upon generation of $(C_5Me_5)Rh(PMe_3)$ in the presence of naphthalene at low temperature. The unsaturated metal intermediate was generated thermally by irradiation of $[(C_5Me_5)Rh(PMe_3)H_2]$ in $[^2H_{14}]$methylcyclohexane to give the alkane activation adduct $[(C_5Me_5)Rh(PMe_3)(C_7D_{13})D]$, followed by warming of the latter in the presence of naphthalene to −30 °C to liberate alkane. ^{31}P NMR spectroscopy shows formation of **2a** (δ 0.72, d, J_{RhP} = 203 Hz). Upon warming to 25 °C, a resonance for **3a** (δ 7.59, d, J_{RhP} = 154
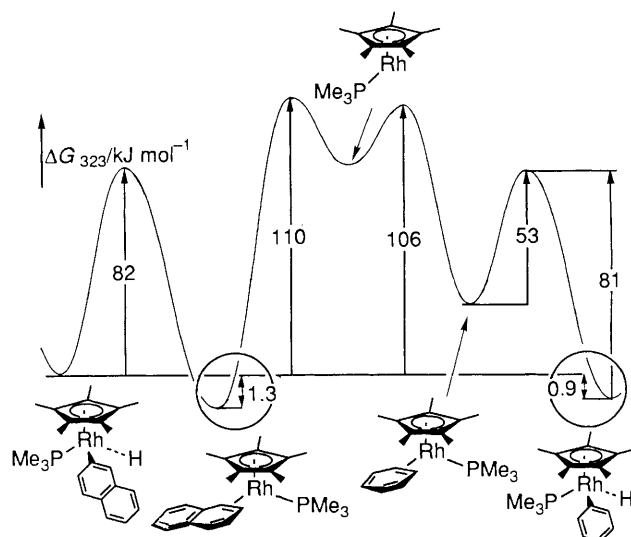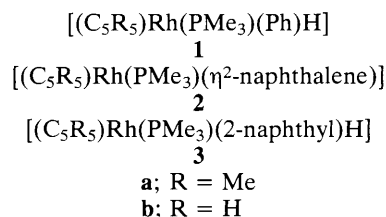

Fig. 3 Free energy diagram for the interaction of benzene and naphthalene with $[(C_5Me_5)Rh(PMe_3)]$ at 323 K. Notice that the major difference between the naphthalene and benzene sides of the diagram lies in the energy of the η^2-arene complexes.¶ The data for the naphthalene–naphthyl hydride complexes are measured by NMR spectroscopy in $[^2H_{12}]$cyclohexane. The data for the benzene–(phenyl)hydride complexes are measured in benzene or $[^2H_8]$tetrahydrofuran either by laser flash photolysis or by NMR spectroscopy. Earlier measurements showed that solvent effects were very small (ref. 3).

$$[(C_5R_5)Rh(PMe_3)(Ph)H]$$
$$\mathbf{1}$$
$$[(C_5R_5)Rh(PMe_3)(\eta^2\text{-naphthalene})]$$
$$\mathbf{2}$$
$$[(C_5R_5)Rh(PMe_3)(2\text{-naphthyl})H]$$
$$\mathbf{3}$$
$$\mathbf{a};\ R = Me$$
$$\mathbf{b};\ R = H$$

Hz) is observed to grow in as the compounds **2a** and **3a** equilibrate (Scheme 3).

In the case of reaction with benzene, $[(C_5Me_5)Rh(PMe_3)(C_2H_4)]$ was employed for the formation of $(C_5Me_5)Rh(PMe_3)$ because it photo-dissociates ethene efficiently. Laser flash photolysis (308 nm) can be used to monitor its reaction with benzene, showing the instantaneous (<1 μs) formation of an intermediate (370 nm) that decays with a lifetime of a few hundred microseconds. Irradiation of the analogous C_5H_5 complex $[(C_5H_5)Rh(PMe_3)(C_2H_4)]$ in benzene gives a similar transient.[5] These intermediates are assigned to the Rh^I η^2-benzene complexes, which decay to give the corresponding phenyl hydride complexes. The rate at which the Rh^I η^2-arene complex converts into the Rh^{III} oxidative addition complex is *ca.* 5 times faster for the more electron rich C_5Me_5 complex than for the C_5H_5 analogue. The temperature dependence of the rate of conversion allows the activation parameters to be extracted (Fig. 2). For the C_5Me_5 complex, $\Delta H^{\ddagger}$ = 46.6 ± 1.3 kJ mol^{-1}, $\Delta S^{\ddagger}$ = −20.4 ± 4.6 J mol^{-1} K^{-1}. The parameters for the C_5Me_5 complex are similar,[5] with $\Delta H^{\ddagger}$ = 48.0 ± 1.8 kJ mol^{-1} and $\Delta S^{\ddagger}$ = −28.8 ± 6.7 J mol^{-1} K^{-1}.

The above information about the thermodynamic stability and kinetic lability of the C_5Me_5 η^2-arene and aryl hydride complexes, combined with previous data,[3] allows the complete comparison of the free energies for benzene and naphthalene activation (Fig. 3). The thermodynamic stability of the (η^2-arene)/(aryl)hydride pairs may be compared relative to the $(C_5Me_5)Rh(PMe_3)$ fragment. The energies of the two (aryl)hydrides differ only marginally, but the η^2-naphthalene complex lies about 28 kJ mol^{-1} lower in energy than

the η^2-benzene complex.¶ As a result, the equilibrium constant for conversion of η^2-arene to (aryl)hydride complex is 0.5 for naphthalene but 3×10^4 for benzene at 50 °C. The kinetic barrier to conversion of (aryl)H to η^2-arene complex is almost identical for naphthalene and benzene, and the transition states lie close in free energy. In contrast, the barrier for the reverse process is ≈ 30 kJ mol^{-1} greater for naphthalene.

These studies demonstrate that (*i*) the equilibria between C–H activation and η^2-coordination of arenes can be controlled by small changes in the ligation, since C_5Me_5 complexes shift equilibria towards Rh^{III} species in both hydrocarbon and fluorocarbon activation,[8] (*ii*) η^2-arene complex formation precedes C–H bond activation, and (*iii*) both the thermodynamic and kinetic effects of C_5H_5 and C_5Me_5 ancillary ligands can be quantified.

¶ The difference in free energy of the η^2-benzene and η^2-naphthalene complexes of 28 kJ mol^{-1} is remarkably close to the upper limiting difference in loss of resonance energy on η^2-coordination of benzene and naphthalene of 21 kJ mol^{-1} (D. J. Brauer and C. Krüger, *Inorg. Chem.*, 1977, **16**, 884).

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