(based on the rate of consumption of B_2H_6 at 11 temperatures in the range 120–180 °C) is 102.6 ± 3.3 kJ mol^{-1}. Again it would be unwise to place too great a significance on these differences, and it is probable that calculations with a larger basis set or incorporating the possibility of tunneling would lead to a revision of the computed values for the activation energy.[7,12]

In summary, a careful reinvestigation of the relative initial rates of decomposition of B_2H_6 and B_2D_6 has led to a value of 2.57 ± 0.65 for the rate-constant ratio k_H/k_D, which disagrees with an earlier experimental value but is close to values obtained in a recent high-level computational study. This important new result therefore removes a potential inconsistency between experiment and computation. Taken in conjunction with the experimentally observed influence of added H_2 in repressing the rate of decomposition of B_2H_6 and in altering the distribution of products, the totality of experimental and computational evidence suggests that the rate-determining step following the symmetric dissociation of diborane is neither simply the formation of $\{B_3H_9\}$ from $\{BH_3\}$ and B_2H_6 nor the subsequent decomposition of $\{B_3H_9\}$ to give $\{B_3H_7\}$ and H_2, but the *concerted* formation and decomposition of $\{B_3H_9\}$ as represented by step 4.

Acknowledgment. We thank Professors J. F. Stanton and W. N. Lipscomb for sending us a preprint of their paper, D. Singh for assistance with the mass spectrometers, and SERC for a maintenance grant (to S.M.L.), and the U.S. Army Research and Standardization Group (Europe) for financial support.

Registry No. B_2H_6, 19287-45-7; B_2D_6, 20396-66-1.

Direct Observation of η^2-Arene Complexes of $[(C_5Me_5)Rh(PMe_3)]$

William D. Jones*,† and Lingzhen Dong

Department of Chemistry, University of Rochester
Rochester, New York 14627

Received June 13, 1989

Over the past few years, there has been substantial progress in studies of the mechanism of activation of aliphatic and aromatic C–H bonds by transition metals.[1] In particular, earlier studies in our group have indicated that arenes coordinate to $[(C_5Me_5)Rh(PMe_3)]$ in an η^2 fashion prior to C–H bond oxidative addition, and that this initial coordination permits the activation of aromatic C–H bonds to compete with aliphatic C–H bond activation.[2] The evidence for η^2-arene coordination relies heavily on indirect experiments (intramolecular isomerization of an aryl deuteride,[2] kinetic isotope effect experiments[3]), as the only direct evidence for arene coordination was with *p*-di-*tert*-butylbenzene at low temperature.[4] We report here the *room temperature* observation of η^2-arene complexes of $[(C_5Me_5)Rh(PMe_3)]$ and an equilibrium between an η^2-arene complex and its aryl hydride counterpart.

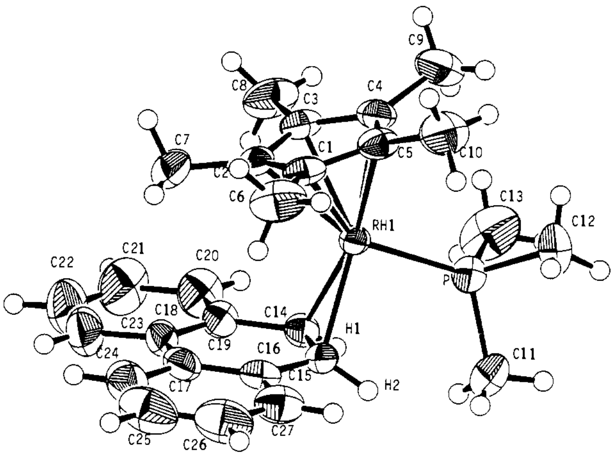
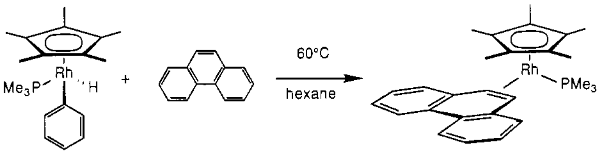


Figure 1. ORTEP drawing of $(C_5Me_5)Rh(PMe_3)(\eta^2$-phenanthrene); ellipsoids shown at the 50% level. Important distances (Å) and angles (deg): Rh–C14, 2.128 (4); Rh–C15, 2.144 (4); C14–C15, 1.428 (6); C14–C19, 1.469 (5); C15–C16, 1.460 (5).

The aryl hydride complex $(C_5Me_5)Rh(PMe_3)(Ph)H$ (**1**) is well established to lose benzene upon heating to 60 °C. In the presence of an excess of another arene, a new aryl hydride complex is formed in high yield. However, when the complex is heated in hexane solution containing 10 equiv of phenanthrene, a single new product is formed for which no hydride resonance is observed by ^1H NMR spectroscopy. Furthermore, the ^{31}P doublet resonance of the starting material at δ 7.90 (J_{P-Rh} = 156 Hz) is replaced by a new doublet at δ 0.31 (J_{P-Rh} = 201 Hz). The upfield shift and increase in coupling constant are typical of the spectral changes characteristic of a change from Rh(III) to Rh(I) in a variety of $CpRhL_n$ and $(C_5Me_5)RhL_n$ complexes.[5] The simplicity of the ^1H NMR spectrum of the arene ligand (four multiplets in the aromatic region and a multiplet at δ 3.56)[6] suggests the symmetrical coordination of the central double bond to the metal center as shown in eq 1.



1

(1)

A single-crystal X-ray structure of this material confirms the above formulation as an η^2-arene complex as shown in Figure 1.[7] The central olefinic double bond of phenanthrene is slightly lengthened compared to free phenanthrene, and the rhodium center lies at a slightly obtuse angle to the planar arene ring. The fused ring system is oriented away from the phosphine ligand, as the other rotamer would superimpose the rings upon the phosphine.

Several other η^2-arene complexes have been structurally characterized, including $[P(Cy)_3]_2Ni(\eta^2$-anthracene),[8] $(PEt_3)_2Pt[\eta^2-C_6(CF_3)_6]$,[9] $[CpRe(CO)_2]_2(\mu-\eta^2-C_6H_6)$,[10] $CpRh(PMe_3)(\eta^2-C_6F_6)$,[11] and a variety of Ag^+(arene)[12] complexes. In

---

[†] Camille and Henry Dreyfus Teacher-Scholar, 1985–1989.

(1) For recent reviews, see: Hill, C. L., Ed. *Activation and Functionalization of Alkanes*; John Wiley and Sons: New York, 1989. Halpern, J. *Inorg. Chim. Acta* **1985**, *100*, 41–48. Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245–269. Shilov, A. E. *Activation of Saturated Hydrocarbons by Transition Metal Complexes*; D. Reidel Publishing Company: Boston, 1984. Jones, W. D.; Feher, F. J. *Acc. Chem. Res.* **1989**, *22*, 91–100.

(2) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1982**, *104*, 4240–4242. Jones, W. D.; Feher, F. J. *Organometallics* **1983**, *2*, 562–563.

(3) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1986**, *108*, 4814–4819.

(4) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *106*, 1650–1663.

(5) Klingert, B.; Werner, H. *Chem. Ber.* **1983**, *116*, 1450–1462.

(6) For $(C_5Me_5)Rh(PMe_3)(\eta^2$-phenanthrene) ^1H NMR ($c-C_6D_{12}$): 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). Anal. Calcd (found) for $RhPC_{27}H_{34}$: C, 65.85 (65.53); H, 6.96 (7.03).

(7) $(C_5Me_5)Rh(PMe_3)(\eta^2$-phenanthrene) crystallizes in monoclinic space group $P2_1/c$ with $Z = 4$, a = 9.922 (4) Å, b = 16.004 (6) Å, c = 15.29 (1) Å, β = 82.12 (5)°. Standard Patterson map solution of the structure and full least-squares refinement of the 2421 data $>3\sigma$ converged with $R_1 = 0.025$, $R_w = 0.036$.

(8) (a) Jonas, K. *J. Organomet. Chem.* **1974**, *78*, 273–279. (b) Brauer, D. J.; Kruger, C. *Inorg. Chem.* **1977**, *16*, 884–891.

(9) Browning, J.; Green, M.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1974**, 97–101. Cobbledick, R. E.; Einstein, F. W. B. *Acta Crystallogr.* **1978**, *B34*, 1849–1853. Browning, J.; Penfold, B. R. *J. Cryst. Mol. Struct.* **1974**, *4*, 335–346.

(10) Heijden, H.; Orpen, A. G.; Pasman, P. *J. Chem. Soc., Chem. Commun.* **1985**, 1576–1578. Cf.: Neithamer, D. R.; Pârkânyi, L.; Mitchell, J. F.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1988**, *110*, 4421–4423.

(11) Perutz, R. N.; Belt, S. T. *J. Chem. Soc., Chem. Commun.* **1989**, in press.

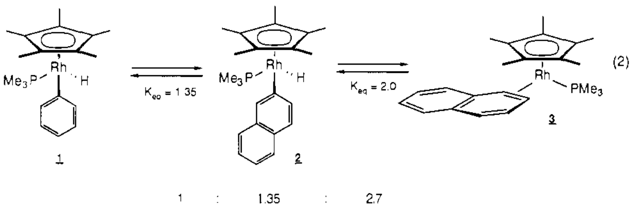
(12) Turner, R. W.; Amma, E. L. *J. Am. Chem. Soc.* **1966**, *88*, 3243–3247. Hall, E. A.; Amma, E. L. *J. Am. Chem. Soc.* **1969**, *91*, 6538–6440. Amma, S. *J. Am. Chem. Soc.* **1969**, *91*, 5745. Turner, R. W.; Amma, E. L. *J. Am. Chem. Soc.* **1966**, *88*, 1877–1882. Turner, R. W.; Amma, E. L. *J. Am. Chem. Soc.* **1963**, *85*, 4046–4047. Hall, W. A.; Amma, E. L. *J. Chem. Soc., Chem. Commun.* **1968**, 622–624.

0002-7863/89/1511-8722$01.50/0

none of these cases is any evidence for competitive C–H bond activation seen. Taube has also recently reported many examples[13] of η^2-arene coordination to $[Ru(NH_3)_5]^{2+}$ and $[Os(NH_3)_5]^{2+}$, and Graham has found evidence for η^2-coordination of arene upon protonation of CpRe(NO)(CO)(Ph).[14]

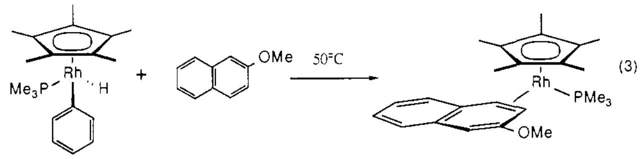
Other fused, polycyclic aromatics also react under conditions of thermal equilibrium to give η^2-arene complexes. Upon heating a 10:10:1 solution of benzene/naphthalene/**1** in hexane for 24 h, three species are observed. The ^{31}P NMR spectrum in C_6D_{12} shows three doublets (δ 7.90, J = 156 Hz; δ 7.63, J = 155 Hz; δ 0.66, J = 203 Hz) in a 1:1.35:2.7 ratio, consistent with the formation of two Rh(III) complexes and one Rh(I) complex (eq 2). One of the Rh(III) complexes can be identified as **1** by comparison with an authentic sample. The second Rh(III) complex is identified as $(C_5Me_5)Rh(PMe_3)$(2-naphthyl)H (**2**) on the basis of 400-MHz ^1H COSY NMR data and independent preparation. The third product is formulated as $(C_5Me_5)Rh(PMe_3)(\eta^2$-naphthalene) (**3**), also on the basis of ^1H NMR data.[15] The ^1H NMR spectrum shows a pair of coupled multiplets at δ 3.629 and 3.213 for the hydrogens on the double bond bound to rhodium. The higher field resonance also couples to one of the aromatic hydrogens at δ 6.570. The η^2-naphthalene/naphthyl hydride isomers can also be formed by direct synthesis. A 1:2 mixture of complexes **2** and **3** is also formed upon reduction of $(C_5Me_5)Rh(PMe_3)$(2-naphthyl)Br[16] with $Na[HB(s\text{-}Bu)_3]$.

Equilibria with 1:1 Benzene:Naphthalene in hexane solvent:



The above observations indicate that under equilibrium conditions *the η^2-naphthalene complex **3** is thermodynamically preferred over the C–H oxidative addition adduct **2**, and that both of these are more stable than the phenyl hydride **1**.* This system is the first example in which reversible arene activation and η^2-coordination are both observed. It is interesting to note that in 1965 Chatt described the chemical behavior of $Ru(dmpe)_2$(naphthyl)H as if the compound were a complex of naphthalene.[17]

We are not certain of the factors that lead to the stabilization of the η^2-naphthalene adducts. Introduction of a 2-methoxy substituent leads to only one product under similar thermal equilibrium conditions, the (3,4-η^2)-methoxynaphthalene complex (eq 3).[18] The electron-donating methoxy group apparently stabilizes even further the η^2-naphthalene complex. We believe that the added stability of these adducts might be associated with the resonance energy that remains following η^2-coordination. With naphthalenes, the fused aromatic system leaves behind a styrene residue, whereas with phenanthrene, a biphenyl moiety remains. Comparison of the heat of hydrogenation of benzene to cyclohexadiene to that for hydrogenation of naphthalene to 1,2-dihydronaphthalene indicates an ~8 kcal/mol preference for the latter reaction.[19] Earlier reports of simple Hückel calculations on the effects of η^2 binding of an arene to a metal support the notion that binding of fused aromatic complexes costs less in terms of resonance energy.[8b] Future studies will continue to investigate the factors that control this equilibrium.



Acknowledgment is made to the U.S. Department of Energy (DE-FG02-86ER13569) for their partial support of this work. W.D.J. also thanks the Camille and Henry Dreyfus Foundations for awards.

Registry No. 1, 81971-46-2; **2**, 123099-42-3; **3**, 123099-43-4; $(C_5Me_5)Rh(PMe_3)(\eta^2$-phenanthrene), 123099-41-2; $(C_5Me_5)Rh(PMe_3)$(2-naphthyl)Br, 123099-44-5; $Na[HB(s\text{-}Bu)_3]$, 67276-04-4; $(C_5Me_5)Rh(PMe_3)((3,4\text{-}\eta^2)$-2-methoxynaphthalene), 123099-45-6.

Supplementary Material Available: Tables listing atomic coordinates, anisotropic thermal parameters, and bond distances and angles for $(C_5Me_5)Rh(PMe_3)(\eta^2$-phenanthrene) (10 pages); calculated and observed structure factors for $(C_5Me_5)Rh(PMe_3)(\eta^2$-phenanthrene) (17 pages). Ordering information is given on any current masthead page.

---

(13) Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1987**, *109*, 1883-1885. Harman, W. D.; Taube, H. *Inorg. Chem.* **1987**, *26*, 2917-2918. Cordone, R.; Taube, H. *J. Am. Chem. Soc.* **1987**, *109*, 8101-8102. Harman, W. D.; Sekine, M.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 2439-2445. Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 5403-5407. Harman, W. D.; Sekine, M.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 5725-5731. Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 7555-7556. Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 7906-7907.

(14) Sweet, J. R.; Graham, W. A. G. *J. Am. Chem. Soc.* **1983**, *105*, 305-306. Sweet, J. R.; Graham, W. A. G. *Organometallics* **1983**, *2*, 135-140.

(15) For $(C_5Me_5)Rh(PMe_3)$(2-naphthyl)H ^1H NMR (c-C_6D_{12}): δ 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 (d, 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), −13.549 (dd, J = 49.8, 32.3 Hz, 1 H). For $(C_5Me_5)Rh(PMe_3)(\eta^2$-naphthalene) ^1H NMR (c-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).

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

(17) Chatt, J.; Davidson, M. M. *J. Chem. Soc.* **1965**, 843-855.

(18) For $(C_5Me_5)Rh(PMe_3)(\eta^2$-2-methoxynaphthalene) ^1H NMR (c-C_6D_{12}): δ 1.187 (d, J = 8.1 Hz, 9 H), 1.310 (d, J = 2.6 Hz, 15 H), 3.043 (dt, J = 7.3, 2.4 Hz, 1 H), 3.678 (dt, J = 7.8, 2.6 Hz, 1 H), 3.721 (s, 3 H), 5.750 (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 NMR (C_6D_{12}): δ 0.39 (d, J = 201 Hz).

(19) Based on heat of formation data for C_6H_6(l), C_6H_8(l), $C_{10}H_8$(s), and $C_{10}H_{10}$(l) from: Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data for Organic Compounds*; Chapman and Hall: New York, 1986. Stull, D. R.; Westrum, E. F.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; John Wiley & Sons: New York, 1969.

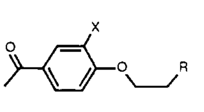
Electronic Effects on the Addition of Double Bonds to Triplet Benzenes: What Is the Rate-Determining Step in Biradical Formation?

Peter J. Wagner* and Masami Sakamoto

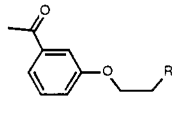
Chemistry Department, Michigan State University
East Lansing, Michigan 48824

Received June 29, 1989

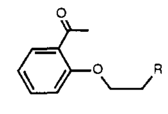
We recently reported that acetophenones containing *o*- or *p*-3-buten-1-oxy substituents undergo rapid internal triplet quenching that leads to 2 + 2 cycloadducts.[1,2] Whereas the reaction of alkenes with excited singlet benzenes has been widely studied,[3] the corresponding triplet reaction is basically unknown. Therefore we have measured rate constants and Arrhenius parameters for a variety of such unsaturated acetophenones in order to establish the nature of the interaction that quenches the excited triplet and leads to product.



1



2



3

---

(1) Wagner, P. J.; Nahm, K. *J. Am. Chem. Soc.* **1987**, *109*, 4404.

(2) Wagner, P. J.; Nahm, K. *J. Am. Chem. Soc.* **1987**, *109*, 6528.

(3) (a) Gilbert, A. *Pure Appl. Chem.* **1980**, *52*, 2669. (b) Mattay, J. *Tetrahedron* **1985**, *41*, 2405.

0002-7863/89/1511-8723$01.50/0