and are much lower than those of the related (η^6-arene)$Cr(CO)_3$ complexes without Fp substituents such as (η^6-$C_{12}H_{10}$)$Cr(CO)_3$.[24,25] Indeed, the substitution of the first Fp group onto the "complexed" ring of (η^6-$C_{12}H_{10}$)$Cr(CO)_3$ causes its formal oxidation potential to decrease by 330 mV while the substitution of a second Fp group on the other rings causes $E^{\circ\prime}$ to decrease by a further 60 mV even over a distance of eight bonds (≈9 Å).[35] These values are consistent with the IR and ^{13}C NMR data (Tables I and II) and unambiguously confirm our earlier suggestion that the Fp substituents in these complexes transfer substantial electron density to the chromium centers, making them very electron rich. Finally, it is interesting to note that the chemical reversibilities of these oxidations and those of other (η^6-arene)$Cr(CO)_3$ complexes[9d,e,25,34] are substantially increased by the addition of activated alumina to the cyclic voltammetry cell, presumably due to the in situ removal of traces of water or other electroactive impurities.

Conclusions

During this study, we have successfully extended the synthetic methodology that we developed earlier for benzene-bridged complexes of (η^5-C_5H_5)$Fe(CO)_2$ to the preparation of a series of polymetallic complexes of biphenyl, terphenyl, naphthalene, and anthracene. Thus, homometallic complexes having two direct Fe–C σ bonds to the aryl and acyl bridging groups in these bimetallic complexes were prepared. Three representative heterometallic complexes of iron and chromium having biphenyl and naphthyl bridging groups were also prepared, and it was established that the iron centers in these heterobimetallic complexes transfer substantial electron density to the π-bonded chromium centers. Unfortunately, because the simple arene- and acyl-bridged complexes were not observed to be oxidized reversibly under the conditions employed, we were not able to ascertain if the addition of increased conjugation to the aromatic bridging groups in these complexes resulted in increased iron–iron electronic interactions in the homometallic complexes.

Acknowledgment. We acknowledge the Natural Sciences and Engineering Research Council of Canada and the University of Alberta for their financial support of this work. We also thank Dr. George B. Richter-Addo for his contributions to the electrochemical studies and Kathy J. Matthews for technical assistance.

Supplementary Material Available: NMR data for (η^6-$C_{12}H_{10}$)$(Cr(CO)_3)_n$ (where n = 1 and 2), $C_{12}H_{10}$, $C_{18}H_{14}$, $C_{10}H_8$, and $C_{14}H_{10}$ recorded in $(CD_3)_2SO$ (2 pages). Ordering information is given on any current masthead page.

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(33) See ref 25 and: (a) Bond, A. M.; Jaouen, G.; Mann, T. F.; Mocellin, E.; Top, S. *Organometallics* **1989**, *8*, 2382–2387. (b) Zoski, C. G.; Sweigart, D. A.; Stone, N. J., Rieger, P. H.; Mocellin, E.; Mann, T. F.; Mann, D. R.; Gosser, D. K.; Doeff, M. M.; Bond, A. M. *J. Am. Chem. Soc.* **1988**, *110*, 2109–2116. (c) Rourke, F.; Crayston, J. A. *J. Chem. Soc., Chem. Commun.* **1988**, 1264–1266. (d) Bullick, J. P.; Boyd, D. C.; Mann, K. R. *Inorg. Chem.* **1987**, *26*, 3084–3086. (e) Stone, N. J.; Sweigart, D. A.; Bond, A. M. *Organometallics* **1986**, *5*, 2553–2555. (f) Doxsee, K. M.; Grubbs, R. H.; Anson, F. C. *J. Am. Chem. Soc.* **1984**, *106*, 7819–7824. (g) Ikeshoji, T.; Parker, V. D. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 1112–1115. (h) Rieke, R. D.; Henry, W. P.; Arney, J. S. *Inorg. Chem.* **1987**, *26*, 420–427. (i) Rieke, R. D.; Milligan, S. N.; Schulte, L. D. *Organometallics* **1987**, *6*, 699–705. (j) Leong, V. S.; Cooper, N. J. *Organometallics* **1987**, *6*, 2000–2002. (k) Connelly, N. G.; Demidowicz, Z.; Kelly, R. L. *J. Chem. Soc., Dalton Trans.* **1975**, 2335–2340. (l) Lloyd, M. K.; McCleverty, J. A.; Connor, J. A.; Jones, E. M. *J. Chem. Soc., Dalton Trans.* **1973**, 1768–1770 and work cited therein.

(34) Hunter, A. D.; Mozol, V.; Cai, S. D. C. *Organometallics*, submitted for publication.

(35) By way of comparison, the addition of a methyl substituent to (η^6-arene)$Cr(CO)_3$ complexes causes $E^{\circ\prime}$ to decrease by approximately 30 mV.[33g,o,p,34]

Multiple η^2-Arene Coordination. Structure and Isomerism of Naphthalene Complexes of $[(C_5Me_5)Rh(PMe_3)]$

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

Received April 16, 1991

The fragment $[(C_5Me_5)Rh(PMe_3)]$ reacts with naphthalene to give both C–H bond activation and η^2-naphthalene complexes. Continued thermal reaction eventually leads to the production of the unusual binuclear species $[(C_5Me_5)Rh(PMe_3)]_2(1,2\text{-}\eta^2\text{-}3,4\text{-}\eta^2\text{-}C_{10}H_8)$, which can be isolated in pure form. The complex crystallizes in monoclinic space group $P2_1/a$ with a = 16.717 (8) Å, b = 16.153 (4) Å, c = 27.721 (8) Å, β = 106.75 (3)°, V = 7167.6 (6.8) Å^3, and Z = 8. The isomerization of the labeled molecule $(C_5Me_5)Rh(PMe_3)$(2-naphthyl)D has been examined and found to proceed intramolecularly within the same ring.

Introduction

Over the past few years, a variety of new π-arene complexes have been discovered in which the metal interacts with a single double bond of the aromatic ligand.[1-4] These complexes have been found to be important precursors in C–H bond oxidative addition reactions.[5,6] Coordination of the metal to the arene alters its reactivity and has found applications in the selective hydrogenation of benzene to cyclohexene.[7] In the present study, a variety of binding modes for naphthalene have been examined, one of which involves the coordination of two metals to the same aromatic ring.

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(1) Belt, S. T.; Duckett, S. B.; Helliwell, M.; Perutz, R. N. *J. Chem. Soc., Chem. Commun.* **1989**, 928–930.

(2) Sweet, J. R.; Graham, W. A. G. *Organometallics* **1983**, *2*, 135–140.

(3) Jones, W. D.; Dong, L. *J. Am. Chem. Soc.* **1989**, *111*, 8722–8723.

(4) 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.

(5) Jones, W. D.; Feher, F. J. *Acc. Chem. Res.* **1989**, *22*, 91–100.

(6) Cordone, R.; Taube, H. *J. Am. Chem. Soc.* **1987**, *109*, 8101–8102.

(7) Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 7906–7907. Harman, W. D.; Schaefer, W. P.; Taube, H. *J. Am. Chem. Soc.* **1990**, *112*, 2682–2685.

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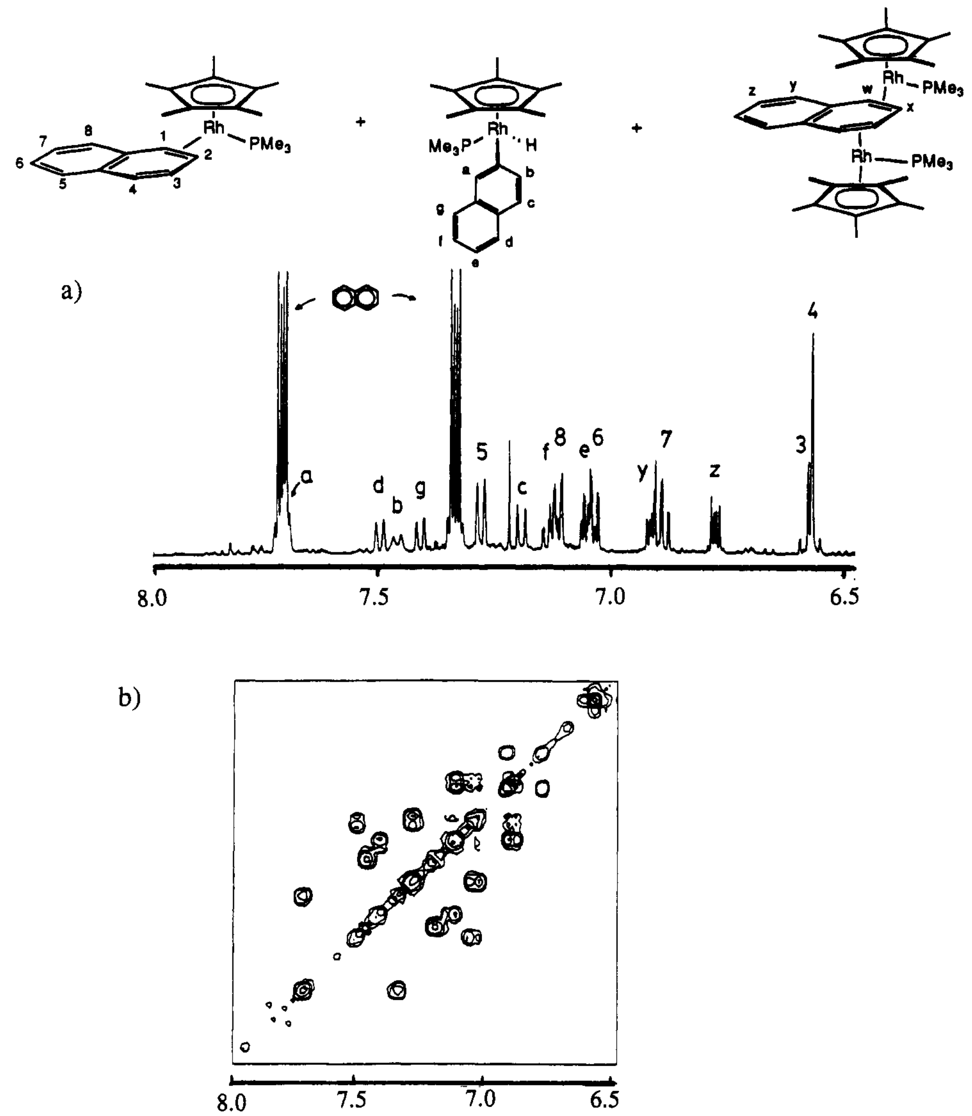

Figure 1. ^1H NMR spectrum of the reaction of 1 with naphthalene: (a) aromatic region (500 MHz, δ 6.5–8.0); (b) COSY of the aromatic region (δ 6.5–8.0).

We have previously reported evidence for the formation of an η^2-benzene complex along the reaction pathway for activation of benzene by $[(C_5Me_5)Rh(PMe_3)]$.[8] Recently, transient laser flash studies have been employed to directly observe the η^2-benzene species, which has a lifetime of ~200 μs at 25 °C.[9] With fused polycyclic aromatics, however, the η^2 complexes are stable, isolable species. With naphthalene in particular, we have found that the C–H activation adduct $(C_5Me_5)Rh(PMe_3)$(2-naphthyl)H and the η^2 complex $(C_5Me_5)Rh(PMe_3)(\eta^2$-naphthalene) are formed upon thermolysis of $(C_5Me_5)Rh(PMe_3)PhH$ for short times in the presence of a large excess of naphthalene.[3]

Results

The complex $(C_5Me_5)Rh(PMe_3)(Ph)H$ serves as a useful thermal precursor for the reactive fragment $[(C_5Me_5)Rh(PMe_3)]$. As mentioned above, naphthalene gives an equilibrium mixture of both η^2 and C–H activation products at short (<24 h) reaction times. Heating a hexane solution of 1 at 51 °C for 15 days in the presence of 5.6 equiv of naphthalene leads to a 2:1 mixture of two major products, $(C_5Me_5)Rh(PMe_3)$(2-naphthyl)H (**2**, 28%) and $(C_5Me_5)Rh(PMe_3)(\eta^2\text{-}C_{10}H_8)$ (**3**, 55%). ^{31}P NMR spectroscopy also provides evidence for a third product 4 (10%; δ 2.20, d, J = 210 Hz), in addition to unreacted 1 (3%) and small quantities of the decomposition product, $(C_5Me_5)Rh(PMe_3)_2$ (2%; δ −2.83, d, J = 217 Hz). The large Rh–P coupling constant in product 4 suggests its formulation as a Rh(I) complex.[10]

The ^1H NMR spectrum of this mixture also provides evidence for not only 2 and 3 but also a third substantial product with C_5Me_5 and PMe_3 ligands. Furthermore, the observation of additional triplet of doublet resonances in the δ 3–4 region of the spectrum suggests the presence of a second η^2-arene complex, assigned to 4. 2D COSY spectroscopy indicates that this minor species has a pair of coupled resonances, one of which overlaps with one resonance of 3. The aromatic region of the spectrum is quite complicated (Figure 1a), but the pair of doublet of doublets at δ 6.906 and 6.776 (assigned to 4) resembles those in free naphthalene and suggests a symmetrical structure for the bound arene. The combined NMR data suggest a structure for 4 in which two $(C_5Me_5)Rh(PMe_3)$ fragments coordinate to adjacent double bonds of naph-

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[8] Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *106*, 1650–1663.

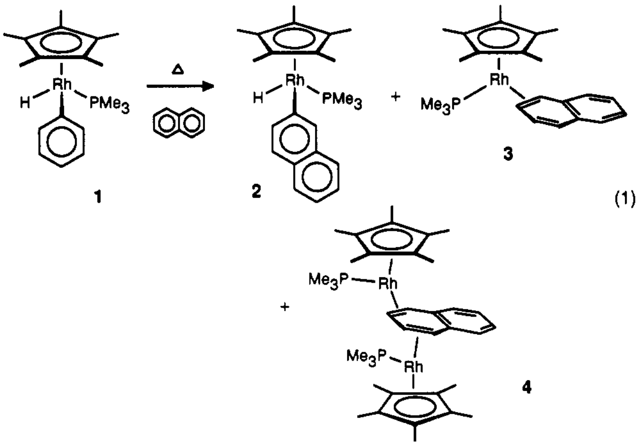
[9] Belt, S. T.; Dong, L.; Duckett, S. B.; Jones, W. D.; Partridge, M.; Perutz, R. N. *J. Chem. Soc., Chem. Commun.* **1991**, 266–269.

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

Table I. Summary of Crystallographic Data for $[(C_5Me_5)Rh(PMe_3)]_2(1,2,3,4\text{-}\eta^2,\eta^2\text{-}C_{10}H_8)$

formula	$Rh_2P_2C_{36}H_{56}$
mol wt	756.59
space group (No.)	$P2_1/a$ (14)
a, Å	16.717 (8)
b, Å	16.153 (4)
c, Å	27.721 (8)
β, deg	106.75 (3)
V, Å^3	7167.6 (6.8)
ρ_{calc}, g cm^{-3}	1.402
Z	8
temp, °C	−75
radiation (monochromator)	Mo, 0.710 73 Å (graphite)
μ, cm^{-1}	10.16
range of transmissn factors	0.78–1.16
$R(F_o)$	0.086
$R_w(F_o)$	0.123
goodness of fit	2.82
largest residual peak in difference map	1.31

thalene on opposite sides of the same ring (eq 1). A COSY spectrum aids in the assignment of resonances of 2–4 (Figure 1b).



(1)

The ability of a second metal to coordinate to the naphthalene in 4 suggested that this complex might be prepared in higher yield if a deficiency of naphthalene were employed in the reaction with 1. This procedure was carried out by taking the initial mixture of 2–4 prepared with an excess of naphthalene and subliming the excess free naphthalene out of the residue. The mixture was then returned to hexane solution and heated to 60 °C for 24 h to reequilibrate the species. Repetition of the sublimation/equilibration sequence led to the precipitation of pure 4 from hexane solution in ~45% isolated yield. The UV–vis spectrum of the product shows two bands in the near-UV at 328 and 375 nm that tail into the visible, giving the material its red color. The naphthalene ligand in both 3 and 4 can be displaced by benzene, demonstrating the reversible nature of this system. A C_6D_{12} solution of 4 containing a 15-fold excess of naphthalene produces a 1:2.2:2.6 mixture of 2, 3, and 4 upon heating at 80 °C for 7 h. The fact that the ratios do not change with further heating indicates that this ratio represents the equilibrium position for the system.

A single-crystal X-ray structural determination of 4 was made to confirm the coordination geometry to the naphthalene ring. The molecule was found to crystallize in monoclinic space group $P2_1/a$ with $Z = 8$, indicating that there are two unique molecules within the asymmetric unit (Table I). Direct methods solution followed by full-matrix least-squares refinement was carried out to give the structure shown in Figure 2. The two metal atoms are located on opposite sides of the naphthalene ring on adjacent double bonds, as suggested by the NMR data. It can also be noted that the C_5Me_5 rings are located over the face of the arene ring, similar to the arrangement previously reported for $(C_5Me_5)Rh(PMe_3)(\eta^2\text{-phenanthrene})$.[3] The two rhodiums lie ~5.1 Å apart.

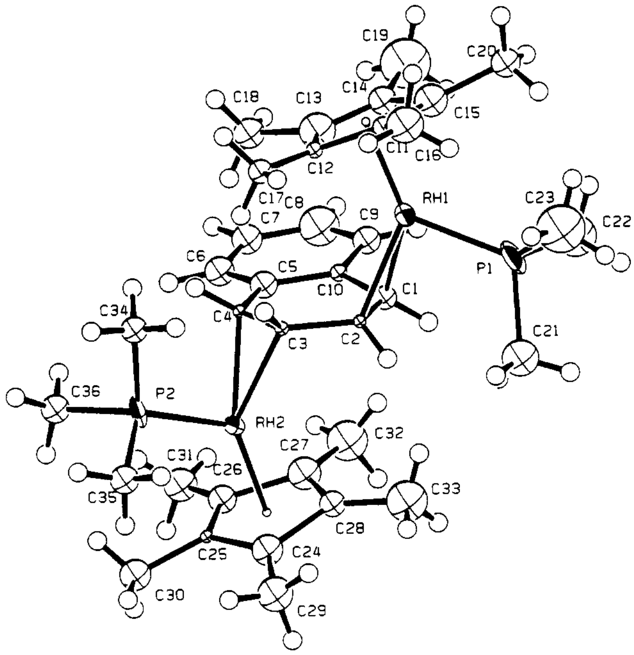


Figure 2. ORTEP drawing of $[(C_5Me_5)Rh(PMe_3)]_2(1,2\text{-}\eta^2\text{-}3,4\text{-}\eta^2\text{-}C_{10}H_8)$. Selected distances: Rh1–C1, 2.17 (4); Rh1–C2, 2.17 (4); Rh2–C3, 2.15 (4); Rh2–C4 2.14 (4); C1–C2, 1.36 (5); C2–C3, 1.46 (5); C3–C4, 1.35 (5); C4–C5, 1.48 (5); C5–C6, 1.40 (6); C5–C10, 1.41 (5); C6–C7, 1.34 (6); C7–C8, 1.37 (6); C8–C9, 1.42 (6); C9–C10, 1.43 (5); C1–C10, 1.45 (5). Dihedral angles: Rh1–naphthalene, 76.3°; Rh2–naphthalene, 66.2°.

The naphthyl deuteride complex 2a was prepared by the reaction of $LiDBEt_3$ with $(C_5Me_5)Rh(PMe_3)$(2-naphthyl)Br. The former complex is prepared by reaction of the corresponding naphthyl Grignard reagent with $(C_5Me_5)Rh(PMe_3)Br_2$ and shows NMR evidence for hindered rotation around the Rh–naphthyl bond, as was seen with other aromatic derivatives.[11] In contrast to the phenyl halide derivatives, however, each rotamer is now distinct in the low-temperature NMR spectrum (see Experimental Section). Another interesting observation is that formation of the Grignard by the addition of 1-naphthyl bromide to magnesium followed by reaction with $(C_5Me_5)Rh(PMe_3)Br_2$ also gives the 2-naphthylrhodium complex! The rearrangement of the 1-naphthyl moiety is believed to occur following its attachment to rhodium, since methylation of the 1-naphthyl Grignard with methyl iodide gives 1-methylnaphthalene as expected. The mechanism of this rearrangement is unknown.

Examination of the initial products of the reaction of $(C_5Me_5)Rh(PMe_3)$(2-naphthyl)Br with $LiDBEt_3$ by ^2H NMR spectroscopy in C_6H_{12} showed four resonances at δ −13.55, 3.16, 6.58, and 7.34 consistent with the initial formation of the four isomers (**2a**, **2b**, **3a**, **3b**) shown in Scheme I. After the mixture is allowed to stand for 8 h at 25 °C, other resonances are observed to grow in the δ 6.9–7.13 region, consistent with the migration of the rhodium to the noncoordinated ring of the naphthalene to form **2c**, **2d**, **3c**, and **3d** (Scheme I). This process is intramolecular, as no 1 is seen when the rearrangement is carried out in the presence of excess C_6H_6. Attempts to

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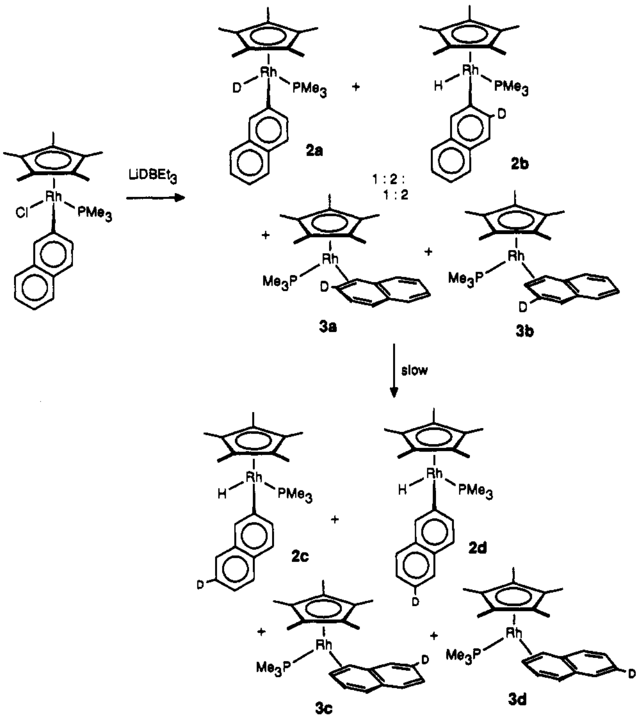
(11) Jones, W. D.; Feher, F. J. *Inorg. Chem.* 1984, *23*, 2376–2388.

Scheme I



monitor the rearrangement of the originally formed 2-naphthyl deuteride **2a** failed due to the inability to synthesize the complex at low temperature.

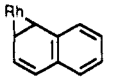
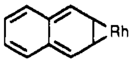
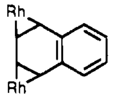
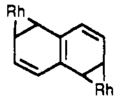
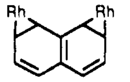
The rearrangement of these isotopomers can also be monitored by ^{31}P NMR spectroscopy. The isotopic perturbation of resonance allowed the determination of the number of deuterium atoms on the η^2-coordinated double bond in compounds **3**. Following addition of LiDBEt$_3$, the ^{31}P NMR spectrum shows two doublets (J = 203 Hz) in a 1:1.3 ratio at δ 0.59 and 0.63 corresponding to **3b** and **3a**, respectively. This ratio changes to 1:3 upon standing for 8 h, consistent with the formation of a 1:1:1:1 ratio of **3a**, **3b**, **3c**, and **3d**. A single doublet is seen at δ 7.63 for the four isotopomers of **2**. Addition of naphthalene-d_8 to the solution followed by brief heating to 80 °C leads to the observation of three doublets in the ^{31}P NMR spectrum at δ 0.59, 0.63, and 0.69 for complexes of **3** in which the η^2-coordinated double bond contains zero, one, or two deuteriums.

Discussion

The ability of [(C$_5$Me$_5$)Rh(PMe$_3$)] to coordinate in an η^2 fashion to arenes is being found to be a general phenomenon, especially in fused polycyclic aromatics. In forming an η^2 complex, the isomer that is formed is that which leaves the greatest opportunity for resonance in the remaining fragment. In the case of naphthalene, the greatest stabilization lies in the formation of a styrene fragment rather than an o-xylylene fragment (2,3-η^2), so that the former species is the only η^2 isomer observed.

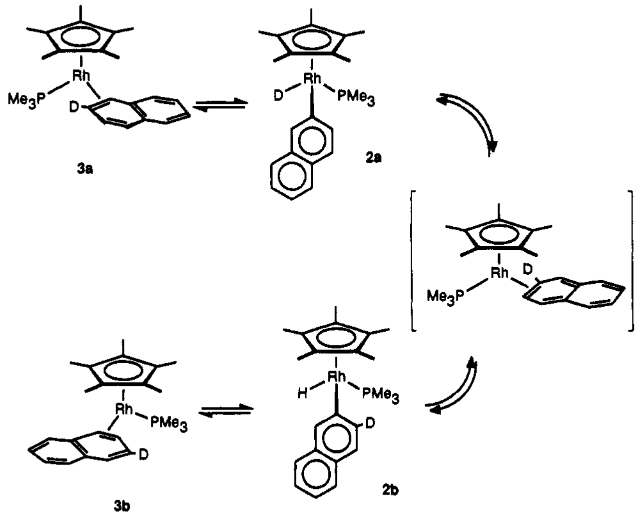
As a consequence of the generally high reactivity of styrene toward transition metals, the formation of **4** should not be so surprising. The second metal must attach to the opposite side of the naphthalene for steric reasons, and the 3,4-η^2 coordination is forced for electronic reasons. Examination of the simple Hückel energies for other bis-η^2 complexes after the procedure used by Krüger et al. for NiL$_2$ complexes[12] indicates that other isomers will be less stable (Table II). It should also be noted that initially only **2** and **3** are formed and that extended reaction times are required for production of the binuclear species **4**. While formation of **4** costs more in terms of resonance energy, the additional stabilization arising from a second rhodium–olefin bond outweighs this expense.

Table II. Resonance Energies for η^2-Arene Complexes (Units of β)[a]

complex	resonance energy of free arene	resonance energy of η^2-arene	$\Delta E_{\text{resonance}}$
	3.68	2.42	1.26
	3.68	1.95	1.73
	3.68	2.00	1.68
	3.68	0.99	2.69
	3.68	0.60	3.08

[a] Energies are in units of β, which is estimated to be 18–20 kcal/mol.

Scheme II



Earlier studies have established the dynamics of the η^2/naphthyl hydride equilibrium.[9] The rearrangement of (C$_5$Me$_5$)Rh(PMe$_3$)(C$_{10}$H$_7$)D provides evidence that the equilibrium between **2** and **3** can also include the less stable o-xylylene isomer (Scheme II). The equilibration with the other ring is much slower, however, providing evidence that the initial isomerization is not dissociative in naphthalene. The overall rate at which naphthalene dissociation occurs is much slower than these isomerization processes, indicating that the isomerizations must occur by intramolecular migration around the naphthalene ring.

Several other examples of bis-η^2 coordination to an arene ring have been reported in the literature. van der Heijden et al. have prepared and structurally characterized the bisrhenium complex [CpRe(CO)$_2$]$_2$(1,2-η^2-3,4-η^2-C$_6$H$_6$).[13]

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(12) Brauer, D. J.; Krüger, C. *Inorg. Chem.* **1977**, *16*, 884–891.

(13) van der Heijden, H.; Orpen, A. G.; Pasman, P. *J. Chem. Soc., Chem. Commun.* **1985**, 1576–1578.

A different mode of coordination was seen in the bistantalum adduct $\{[(t\text{-Bu})_3SiO]_3Ta\}_2(1,2\text{-}\eta^2\text{-}4,5\text{-}\eta^2\text{-}C_6H_6)$, with the two metals occupying sites opposite one another on the arene ring.[14] The bonding of each η^2-carbon to the metal was not symmetrical, however, a feature that may reflect the instability of this bonding mode. More recently, Harman and Taube have observed the formation of $\{[Os(NH_3)_5]_2(1,2\text{-}\eta^2\text{-}3,4\text{-}\eta^2\text{-}C_6H_6)\}^{4+}$[15] and the naphthalene complex $\{[Os(NH_3)_5][Ru(NH_3)_5](1,2\text{-}\eta^2\text{-}3,4\text{-}\eta^2\text{-}C_{10}H_8)\}^{4+}$.[16] The proposed structure for the latter complex is analogous to that determined in the present study for 4. It is also worth noting that while the osmium dinuclear species was thermodynamically preferred, the mononuclear species was the kinetically formed material just as observed in the current system.

Experimental Section

All solvents and compounds were handled in an inert atmosphere of nitrogen either in a Vacuum Atmospheres Dry-Lab or on a high-vacuum manifold. $(C_5Me_5)Rh(PMe_3)Cl_2$ and $(C_5Me_5)Rh(PMe_3)PhH$ were prepared as previously described.[8] Naphthyl Grignards were prepared from 1-bromonaphthalene or 2-bromonaphthalene and magnesium metal using standard procedures. $LiDBEt_3$ was obtained from Aldrich Chemical Co. NMR spectra were recorded on a Bruker AMX-400 NMR spectrometer.

Reaction of $(C_5Me_5)Rh(PMe_3)PhH$ with Naphthalene. 1 (0.043 g, 0.11 mmol) was dissolved in 8 mL of hexane and 0.080 g of naphthalene (0.62 mmol) added. The mixture was heated in a glass ampule at 51 °C for 15 days. The solvent was evaporated and excess naphthalene removed by sublimation. ^{31}P and ^1H NMR spectroscopy showed three major products in a 2:1:0.18 ratio which were assigned to $(C_5Me_5)Rh(PMe_3)(\eta^2\text{-naphthalene})$, $(C_5Me_5)Rh(PMe_3)(2\text{-naphthyl})H$, and $[(C_5Me_5)Rh(PMe_3)]_2(\eta^2,\eta^2\text{-naphthalene})$. Small amounts of $(C_5Me_5)Rh(PMe_3)PhH$ and $(C_5Me_5)Rh(PMe_3)_2$[17] were also observed.

Preparation of $[(C_5Me_5)Rh(PMe_3)]_2(1,2\text{-}\eta^2\text{-}3,4\text{-}\eta^2\text{-}C_{10}H_8)$. A hexane solution (10 mL) of $(C_5Me_5)Rh(PMe_3)PhH$ (210 mg, 0.54 mmol) and naphthalene (0.825 g, 6.4 mmol) was heated at 70 °C for 36 h. The solvent was then removed under vacuum and the excess naphthalene sublimed from the residue (35 °C). The red solid that remained was redissolved in 10 mL of hexane and the mixture reheated for 12 h. The excess naphthalene was again sublimed from the mixture and the residue taken up in 3–5 mL of hexane. Upon cooling to −35 °C, an orange precipitate formed and was collected. Isolated yield: 89 mg (44%). The mother liquor was found to contain more product of lower purity. ^1H NMR (C_6D_{12}): δ 1.174 (d, J = 8.5 Hz, 18 H), 1.436 (d, J = 2.7 Hz, 30 H), 3.016 (dt, J = 7.4, 2.5 Hz, 2 H), 3.222 (dt, J = 7.4, 2.3 Hz, 2 H), 6.776 (m, 2 H), 6.906 (m, 2 H). ^{31}P NMR (C_6D_{12}): δ 2.20 (d, J = 210 Hz). ^{13}C NMR (C_6D_6): δ 10.29 (s, C_5Me_5), 16.24 (d, J = 24.7 Hz, PMe_3), 41.03 (d, J = 15.1 Hz, η^2-CH), 46.78 (d, J = 13.6 Hz, η^2-CH), 96.01 (t, J = 3.4 Hz, C_5Me_5), 118.54 (s, CH), 122.98 (s, CH), 140.62, (s, C). Anal. Calcd (Found) for $Rh_2P_2C_{36}H_{56}$: C, 57.15, (58.15); H, 7.46 (7.47); P, 8.19 (9.49).

Reaction of $[(C_5Me_5)Rh(PMe_3)]_2(1,2\text{-}\eta^2\text{-}3,4\text{-}\eta^2\text{-}C_{10}H_8)$ with Naphthalene. A 2.6-mg (0.0034-mmol) sample of $[(C_5Me_5)Rh(PMe_3)]_2(1,2\text{-}\eta^2\text{-}3,4\text{-}\eta^2\text{-}C_{10}H_8)$ and 7 mg (0.055 mmol) of naphthalene were dissolved in 0.45 mL of C_6D_{12} in an NMR tube, and the solution was heated to 80 °C for 7 h. A ^{31}P NMR spectrum showed three doublets at δ 7.63 (J = 155 Hz), 0.66 (J = 203 Hz), and 2.20 (J = 210 Hz) in a 1:2.2:2.6 ratio. The solution was heated an additional 8 h. A ^{31}P NMR spectrum showed the same ratio of products.

Preparation of $(C_5Me_5)Rh(PMe_3)(2\text{-naphthyl})Br$. $(C_5Me_3)Rh(PMe_3)Br_2$ (0.120 g, 0.25 mmol) was dissolved in 15 mL of anhydrous THF under nitrogen. 2-Naphthylmagnesium bromide/THF (3.4 mL, 0.32 M, 1.09 mmol) was added dropwise with a syringe at room temperature over 10 min. The dark red solution gradually turned orange. The solution was stirred for 2 h, and 0.8 mL of a saturated solution of NH_4Br was then added to quench the Grignard. The solvent was removed under reduced pressure and the product extracted with methylene chloride and filtered through a fine sintered glass filter. The red orange solution was reduced to 0.5 mL and chromatographed on a silica gel TLC plate. The first orange band that eluted with 2% THF/CH_2Cl_2 was the desired product. Orange crystals were recrystallized from CH_2Cl_2/hexane in 42% yield. Anal. Calcd (Found) for $C_{23}H_{31}BrPRh$: C, 53.00 (53.01); H, 6.00 (5.92). ^1H NMR (C_6D_6): 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) (ortho hydrogens not observed due to broadening from hindered rotation.[11] ^1H 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, 1 H), 7.605 (br d, 1 H), 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. The chloro analogue, $(C_5Me_5)Rh(PMe_3)(2\text{-naphthyl})Cl$, was prepared similarly.

Reaction of $(C_5Me_5)Rh(PMe_3)Br_2$ with (1-Naphthyl)MgBr/THF. $(C_5Me_5)Rh(PMe_3)Br_2$ (0.095 g, 0.20 mmol) was dissolved in 30 mL of THF and 3.5 mL of (1-naphthyl)magnesiumbromide/THF (0.12 M, 0.40 mmol) added dropwise via syringe. The reaction underwent a color change from dark red to orange upon stirring for 30 min. After 1 h, one drop of the crude product was taken out for analysis (100% yield of $(C_5Me_5)Rh(PMe_3)(2\text{-naphthyl})Br$ by ^1H NMR spectroscopy). After 3-h reaction, the solution was quenched with a saturated aqueous NH_4Br solution (0.2 mL). Following removal of the solvent, a ^1H NMR spectrum showed that there was 90% of $(C_5Me_5)Rh(PMe_3)(2\text{-naphthyl})Br$ and 10% of starting material $(C_5Me_5)Rh(PMe_3)Br_2$ in the product. Following TLC on silica gel with 2% THF/CH_2Cl_2 the orange compound was isolated in 51% yield. NMR data showed that it was the 2-naphthyl complex.

Reaction of $(C_5Me_5)Rh(PMe_3)(2\text{-naphthyl})Br$ with $LiDBEt_3$. A solution of 29.2 mg of $(C_5Me_5)Rh(PMe_3)(2\text{-naphthyl})Br$ (0.056 mmol) in 2 mL of THF was treated with 70 μL (0.07 mmol) of a 1 M solution of $LiDBEt_3$. After the mixture was stirred for 20 min, the solvent was removed and the residue allowed to stand for 2 h. The red oil was then taken up in 0.5 mL of C_6H_{12} and placed in an NMR tube. ^2H and ^{31}P NMR spectra were recorded over the next few hours, as described in the text. A similar reaction containing 50 μL of C_6H_6 showed no incorporation of benzene after standing for 8 h at 25 °C. A 7-mg portion of naphthalene-d_8 was added and the solution heated to 80 °C for 15 min. ^{31}P NMR spectroscopy showed appearance of three doublets in the η^2 region as described in the text.

X-ray Structural Determination of $[(C_5Me_5)Rh(PMe_3)]_2(1,2\text{-}\eta^2\text{-}3,4\text{-}\eta^2\text{-}C_{10}H_8)$. A small red crystal of the compound was mounted on a glass fiber and coated with epoxy. Initial cell determination was carried out with 25 centered reflections with values of χ between 5 and 75° and values of θ between 5 and 15°. Cell reduction suggested a C-centered orthorhombic cell, but axial photographs and examination of a small hemisphere of data were consistent only with $2/m$ Laue symmetry. The symmetry was therefore lowered to a smaller, *primitive* monoclinic cell. Data collection and reduction[18] was carried out with the

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(14) Neithamer, D. R.; Parkanyi, L.; Mitchell, J. F.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1988**, *110*, 4421–4423.

(15) Harman, W. D.; Taube, H. *Inorg. Chem.*, **1987**, *26*, 2917–2918.

(16) Harman, W. D.; Taube, H. *J. Am. Chem. Soc.*, **1988**, *110*, 7555–7556.

(17) Werner, H. *Chem. Ber.* **1983**, *116*, 1450–1462.

(18) $R_1 = \{\sum||F_o| - |F_c||\}/\{\sum|F_o|\}$; $R_2 = [\sum w(|F_o| - |F_c|)^2]^{1/2}/\{\sum wF_o^2\}$, where $w = [\sigma^2(F_o) + (\rho F_o^2)^2]^{1/2}$ for the non-Poisson contribution weighting scheme. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$. Source of scattering factors f_o, f', f'': Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.2B and 2.3.1.

parameters specified in Table S-1 (see supplementary material). A Z value of 8 requires the presence of two independent molecules per asymmetric unit, and a direct-methods solution revealed the positions of the four unique rhodium atoms. The structure was expanded using the DIRDIF program supplied by the Molecular Structure Corp., whose programs were used for further refinement of the structure. Full-matrix least-squares isotropic refinement of the non-hydrogen atoms was followed by a differential absorption correction using the program DIFABS, after which anisotropic refinement of the Rh and P atoms led to convergence. Hydrogen atoms were placed in idealized positions based on peaks found in a difference Fourier map. Data collection on four other crytals was also undertaken, carefully optimizing data collection parameters by analyzing scan profiles, in an effort to obtain an improved structure. While all data sets gave the same solution, the quality of the refinement was no better than that reported here.

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Supplementary Material Available: Complete lists of data collection parameters, bond lengths and angles, atomic coordinates, thermal parameters, and least-squares planes (20 pages); a table of calculated and observed structure factors (19 pages). Ordering information is given on any current masthead page.

Insertion of Isocyanides into the Zr–C Bond of Ruthenium/Zirconium Dimetalloalkenes. Spectroscopic and Structural Comparisons of the η^2-Iminoacyl Complexes $Cp(PMe_3)_2RuCH{=}CRC(N^tBu)ZrClCp_2$ (R = H vs R = Me) and Kinetics of Isomerization of a Thermodynamically Unstable η^2-Iminoacyl Complex

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The reaction of $Cp(PMe_3)_2RuCH{=}CHZrClCp_2$ with ^tBuNC produces an η^2-iminoacyl complex, $Cp(PMe_3)_2RuCH{=}CHC(N^tBu)ZrClCp_2$. The initially formed isomer of this compound is the "N-outside" isomer (**2Hk**), where the N-donor portion of the η^2-iminoacyl ligand is on the outside position of the three ligation sites of the Cp_2Zr moiety. This kinetic isomer cleanly rearranges to the thermodynamic "N-inside" isomer (**2Ht**). Activation parameters determined for this rearrangement are $\Delta H^{\ddagger} = 19.9 \pm 0.6$ kcal mol^{-1}, $\Delta S^{\ddagger} = -3.4 \pm 2.2$ cal K^{-1} mol^{-1}, and $\Delta G^{\ddagger}(298\text{ K}) = 20.9$ kcal mol^{-1}. Spectroscopic and crystallographic data for **2Ht** indicate a significant contribution from a zwitterionic resonance form that is facilitated by the disparate electronic properties of the electron-rich ruthenium and the electron-deficient zirconium moieties. The reaction of ^tBuNC with the analogous methylated dimetalloalkene $Cp(PMe_3)_2RuCH{=}C(CH_3)ZrClCp_2$ gives the η^2-iminoacyl complex $Cp(PMe_3)_2RuCH{=}C(CH_3)C(N^tBu)ZrClCp_2$ (**2Me**). Spectroscopic and crystallographic data for **2Me** indicate that the presence of a single methyl group has a profound influence on the structural and electronic properties of this η^2-iminoacyl complex, compared to **2Ht**. In contrast to **2Ht**, the metals and the organic bridging group in **2Me** are twisted out of planarity in order to avoid an unfavorable interaction of the methyl group and the ^tBu group. Spectroscopic and structural data suggest negligible contribution from the zwitterionic resonance form in this compound, due to steric inhibition of resonance. The reaction of the less sterically demanding isocyanide MeNC with $Cp(PMe_3)_2RuCH{=}C(R)ZrClCp_2$ (R = H, CH_3) gives $Cp(PMe_3)_2RuCH{=}CHC(NMe)ZrClCp_2$ (**3H**) and $Cp(PMe_3)_2RuCH{=}C(CH_3)C(NMe)ZrClCp_2$ (**3Me**). Spectroscopic data for **3H** and **3Me** and structural data for **3Me** indicate a contribution from a zwitterionic resonance form for both of these η^2-iminoacyl complexes. Crystallographic data for **2Ht**: orthorhombic space group $Pnma$, $a = 16.640$ (3) Å, $b = 13.936$ (3) Å, $c = 13.290$ (3), $V = 3082$ (2) Å^3, $Z = 4$. Crystallographic data for **2Me**: monoclinic space group $P2_1/c$, $a = 13.386$ (3) Å, $b = 22.514$ (6) Å, $c = 10.639$ (3), $\beta = 91.89$ (2)°, $V = 3205$ (3) Å^3, $Z = 4$. Crystallographic data for **3Me**: monoclinic space group $P2_1/n$, $a = 13.031$ (3) Å, $b = 14.880$ (4) Å, $c = 15.594$ (3), $\beta = 108.08$ (2)°, $V = 2874$ (2) Å^3, $Z = 4$.

Insertion of small molecules into metal–carbon bonds is a reaction of fundamental importance in organometallic chemistry.[1] The most thoroughly investigated reaction of this type, migratory insertion of CO into a metal–alkyl bond to form a metal acyl[2] complex, is a critical step in several homogeneous catalytic reactions such as hydroformylation. A reaction that is closely related to the migratory insertions of CO is the reaction of metal alkyl

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(1) For reviews of the CO insertion reaction, see: (a) Alexander, J. J. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Patai, S., Ed.; Wiley: New York, 1985; Vol. 2; pp 339–400. (b) Calderazzo, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 299–311. (c) Wojcicki, A. *Adv. Organomet. Chem.* **1973**, *11*, 87–145. (d) Kuhlmann, E. J.; Alexander, J. J. *Coord. Chem. Rev.* **1980**, *33*, 195–225.

(2) For a review of η^2-acyl and η^2-iminoacyl complexes, see: Durfee, L. D.; Rothwell, I. P. *Chem. Rev.* **1988**, *88*, 1059–1079.

0276-7333/92/2311-0876$03.00/0