C−C Activation in Biphenylene. Synthesis, Structure, and Reactivity of $(C_5Me_5)_2M_2$(2,2′-biphenyl) (M = Rh, Co)

Christophe Perthuisot, Brian L. Edelbach, Deanna L. Zubris, and William D. Jones*

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

Received December 17, 1996⊗

Carbon−carbon bond cleavage of biphenylene was achieved with $(C_5Me_5)M(C_2H_4)_2$ (M = Rh, Co) to give the bimetallic species $(C_5Me_5)_2M_2$(2,2′-biphenyl). The isomorphous solid state X-ray structures of these complexes showed the biphenyl substrate to be σ-coordinated to one metal and η^4-bound to the other. These complexes display dynamic behavior, interchanging the σ- and π-bonding. Variable-temperature NMR studies were performed on both binuclear species, and the energy barrier for interconversion of the two (C_5Me_5) fragments was calculated to be $\Delta G^\ddagger$ (350 K) = 16.8 kcal/mol and $\Delta G^\ddagger$ (248 K) = 11.4 kcal/mol for the rhodium and cobalt complexes, respectively. $(C_5Me_5)_2Rh_2$(2,2′-biphenyl) reacted with CO to give $(C_5Me_5)Rh(CO)_2$ and $(C_5Me_5)Rh(CO)$(2,2′-biphenyl), while the cobalt analog gave $(C_5Me_5)Co(CO)_2$ and fluorenone. $(C_5Me_5)_2Co_2$(2,2′-biphenyl) gave $(C_5Me_5)Co(PMe_3)_2$ and $(C_5Me_5)Co(PMe_3)$(2,2′-biphenyl) when reacted with PMe_3, as determined by X-ray crystallography of the latter complex. Both complexes were found to be resistant to hydrogenation.

Introduction

The cleavage of unreactive carbon−carbon bonds by oxidative addition to a transition metal center remains an elusive target in organometallic chemistry. A few examples have appeared over the past 20 years in which unstrained C−C bonds are cleaved, but these typically rely upon formation of an η^5-C_5R_5 or η^6-C_6R_6 ring[1] or an intramolecular addition in which the C−C bond is "forced" to react with the metal by proximity.[2] Electrophilic metals can undergo β-alkyl migration,[3] and there are many examples of C−C cleavage in strained ring systems.[4] Metal insertion into the C−C single bond of cyclopentadiene has even been observed.[5]

We recently reported the ring cleavage of biphenylene by $(C_5Me_5)Rh(PMe_3)(Ph)H$[6] and observed that the C−C inserted complex $(C_5Me_5)Rh(PMe_3)$(2,2′-biphenyl) was too thermally stable to undergo hydrogenolysis of the coordinated biphenyl. We, therefore, became interested in studying the activation of biphenylene by a complex with a more labile ligand in place of the PMe_3 group, thus providing an additional vacant site for coordination of hydrogen and the possible reductive elimination of the hydrogenated substrate.

$(C_5Me_5)Rh(C_2H_4)_2$ (**1**) can lose ethylene to provide two coordination sites and is known to activate C−H bonds,[7] making this complex a prime candidate for C−C activation. Reactions carried out with **1** or its analog $(C_5Me_5)Co(C_2H_4)_2$ (**2**) and thiophenes have demonstrated the ability of these complexes to perform C−S activation (Scheme 1).[8] The results described here indicate that C−C cleavage can be carried out in a similar fashion.

Results

Synthesis and Characterization of $(C_5Me_5)_2M_2$(2,2′-biphenyl). Both $(C_5Me_5)Rh(C_2H_4)_2$ (**1**)[9] and $(C_5Me_5)Co(C_2H_4)_2$ (**2**)[10] were prepared according to literature methods, complex **1** by reaction of the dimer $[(C_5Me_5)RhCl_2]_2$ with ethylene in the presence of sodium carbonate and complex **2** by reaction of $[(C_5Me_5)CoI_2]_2$ with ethylene in the presence of zinc. Both were purified by sublimation before use.

The reaction of **1** with biphenylene was examined in n-octane-d_{18}.[11] Biphenylene reacts with 2 equiv of (C5-

---

⊗ Abstract published in *Advance ACS Abstracts,* April 15, 1997.

[1] Eilbracht, P. *Chem. Ber.* **1976**, *109*, 1429. Crabtree, R. H.; Dion, R. P.; Gibboni, D. J.; McGrath, D. V.; Holt, E. M. *J. Am. Chem. Soc.* **1986**, *108*, 7222−7227. Benfield, F. W. C.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1974**, 1324−1331. Jones, W. D.; Maguire, J. A. *Organometallics* **1987**, *6*, 1301−1311. Hemond, R. C.; Hughes, R. P.; Locker, H. B. *Organometallics* **1986**, *5*, 2391−2392. Kang, J. W.; Moseley, K.; Maitlis, P. J. *J. Am. Chem. Soc.* **1969**, *91*, 5970−5977.

[2] Suggs, J. W.; Jun, C.-H. *J. Chem. Soc., Chem. Commun.* **1985**, 92−93. Gozin, M.; Weisman, A.; Ben-David, Y.; Milstein, D. *Nature* **1993**, *364*, 699−701. Gozin, M.; Aizenberg, M.; Liou, S.-Y.; Weisman, A.; Ben-David, Y.; Milstein, D. *Nature* **1994**, *370*, 42−44.

[3] Watson, P. L.; Roe, D. C. *J. Am. Chem. Soc.* **1982**, *104*, 6471−6473. Bunel, E.; Burger, B. J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 976−978.

[4] Adams, D. M.; Chatt, J.; Guy, R. G.; Sheppard, N. *J. Chem. Soc.* **1961**, 738−742. Bailey, N. A.; Gillard, R. D.; Keeton, M.; Mason, R.; Russell, D. R. *J. Chem. Soc., Chem. Commun.* **1966**, 396−398. McQuillin, F. J.; Powell, K. C. *J. Chem. Soc., Dalton Trans.* **1972**, 2123−2129. Barretta, A.; Cloke, F. G. N.; Feigenbaum, A.; Green, M. L. H.; Gourdon, A.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1981**, 156−158. Baretta, A.; Chong, K. S.; Cloke, F. G. N.; Feigenbaum, A.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1983**, 861−864. Flood, T. C.; Statler, J. A. *Organometallics* **1984**, *3*, 1795−1803. Eisch, J. J.; Piotrowski, A. M.; Han, K. I.; Krüger, C.; Tsay, Y. H. *Organometallics* **1985**, 224−231. Lu, Z.; Jun, C.-H.; de Gala, S. R.; Sigalas, M.; Eisenstein, O.; Crabtree, R. H. *J. Chem. Soc., Chem. Commun.* **1993**, 1877−1880. Schwager, H.; Spyroudis, S.; Vollhardt, K. P. C. *J. Organomet. Chem.* **1990**, *382*, 191−200. Murakami, M.; Amii, H.; Shigeto, K.; Ito, Y. *J. Am. Chem. Soc.* **1996**, *118*, 8285−8290.

[5] Suzuki, H.; Takaya, Y.; Takemori, T. *J. Am. Chem. Soc.* **1994**, *116*, 10779−10780.

[6] Perthuisot, C.; Jones, W. D. *J. Am. Chem. Soc.* **1994**, *116*, 3647−3648.

[7] Seiwell, L. P. *J. Am. Chem. Soc.* **1974**, *96*, 7134−7135.

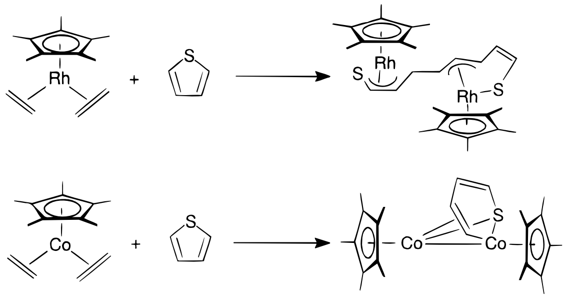
[8] (a) Jones, W. D.; Chin, R. M. *J. Am. Chem. Soc.* **1992**, *114*, 9851−9858. (b) Jones, W. D.; Chin, R. M. *J. Organomet. Chem.* **1994**, *472*, 311−316. (c) Jones, W. D.; Chin, R. M. *Organometallics* **1992**, *11*, 2698−2700.

[9] Maitlis, P. M.; Kang, J. W.; Moseley, K. J. *J. Chem. Soc. A* **1970**, 2875.

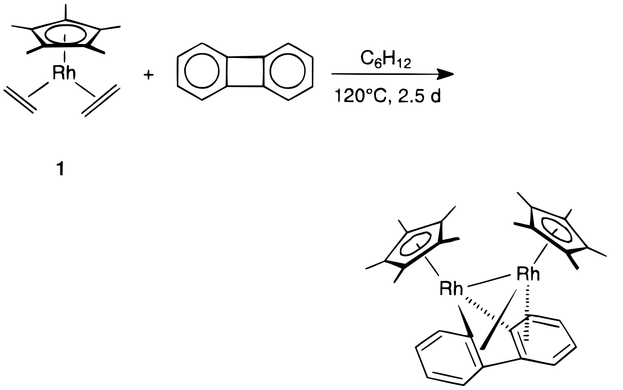
[10] Nicholls, J. C.; Spencer, J. L. *Inorg. Synth.* **1990**, *28*, 278−280.

S0276-7333(96)01059-X CCC: $14.00

Scheme 1



$Me_5)Rh(C_2H_4)_2$ at 115 °C to give the new bimetallic species $(C_5Me_5)_2Rh_2(2,2'\text{-biphenyl})$ (**3**, eq 1). Periodic removal of ethylene was necessary for the reaction to go to completion. Deep purple crystals of **3** were obtained after a few days at room temperature (83% yield). Preparative-scale reactions were carried out in cyclohexane.



1

3

(1)

Complex **3** was fully characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopies, X-ray crystallography, and elemental analysis. The ^1H NMR spectrum showed the presence of two distinct C_5Me_5 groups and an ABCD pattern for the biphenylene, and a ^{13}C-jmod experiment revealed the presence of a quaternary carbon coupled to both rhodium atoms at δ 149.27 (dd, J = 44.8, 14.8 Hz), consistent with the structure where the coordinated biphenyl exhibits σ-coordination to one of the metal centers and η^4-coordination to the other.

The solid state structure of **3** was determined by single-crystal X-ray diffraction, confirming the solution NMR structure (Figure 1). The complex was found to crystallize in the monoclinic space group $P2_1/c$, with Z = 8 and two independent molecules in the asymmetric unit. Small distortions due to steric interactions between the two $(C_5Me_5)Rh$ fragments can be observed. Rh(2) is 4.7° out of the biphenyl plane (mean deviation 0.015 Å), and a 2.8° angle exists between the planar biphenyl and the C_5Me_5 ring attached to Rh(2). The Rh(1)−Rh(2) distance was found to be 2.683 (2) Å, consistent with a single metal−metal bond. Data collection parameters are given in Table 1, and selected bond distances and angles are listed in Table 2.

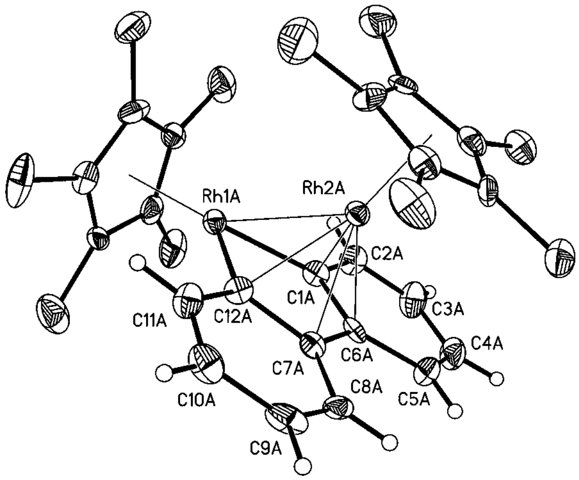
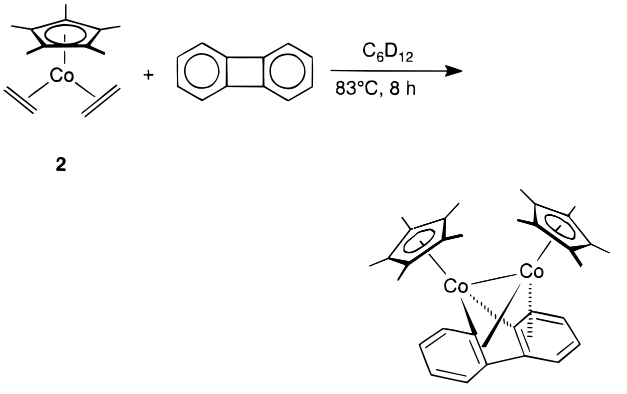


Figure 1. ORTEP drawing of $(C_5Me_5)_2Rh_2(2,2'\text{-biphenyl})$ (**3**), showing the ellipsoids at the 50% probability level.

The reaction of $(C_5Me_5)Co(C_2H_4)_2$, **2**, with 1 equiv of biphenylene in cyclohexane-d_{12} was monitored by ^1H NMR spectroscopy at 83 °C. The reaction went to completion in ~8 h, and the ^1H NMR spectrum exhibited two doublets (δ 7.469, 8.357) and two triplets (δ 7.003, 7.138) in the aromatic region, suggesting that C−C cleavage had occurred to generate $(C_5Me_5)_2Co_2(2,2'\text{-biphenyl})$ (**4**, eq 2, 75% yield). Only one C_5Me_5 resonance was observed, which integrated for 30 hydrogens, suggesting that the two C_5Me_5 fragments were rapidly interconverting with each other (*vide infra*). A ^{13}C-jmod spectrum revealed the presence of two quaternary carbons with chemical shifts similar to those of **3** (δ 116.35, 144.20).



2

4

(2)

A single-crystal X-ray structure of complex **4** confirmed the similarity of the cobalt and rhodium products (Figure 2). The complex is isomorphous with the rhodium derivative, crystallizing in space group $P2_1/c$, with Z = 8. As in the rhodium system, the cobalt is slightly out of the metallacyclopentadiene plane and the biphenyl system is almost coplanar with the opposite C_5Me_5 ring. The cobalt−cobalt bond distance is 2.483 Å, typical of a Co−Co single bond. Selected distances are included in Table 2 for comparison with **3**.

Variable-Temperature NMR. Complexes **3** and **4** were found to be fluxional, the two $(C_5Me_5)M$ groups

---

(11) The reaction of $(C_5Me_5)Rh(C_2H_4)_2$ with biphenylene was first examined in cyclohexane-d_{12}. After 18 h at 83 °C the ^1H NMR spectrum revealed the presence of benzene and the partial disappearance of the biphenylene resonances. The NMR data seemed consistent with the catalytic conversion of biphenylene to benzene, but more careful examination of the reaction demonstrated that the observations were the result of H/D exchange[7] between a small quantity of C_6D_6 in the commercially obtained cyclohexane-d_{12} and the free biphenylene! In fact, all sources of C_6D_{12} examined showed the presence of trace quantities of C_6D_6, as this solvent is synthesized commercially by the catalytic deuteration of C_6D_6.

Table 1. Data Collection Parameters for $(C_5Me_5)_2Rh_2$(2,2′-biphenyl) (3), $(C_5Me_5)_2Co_2$(2,2′-biphenyl) (4), and $(C_5Me_5)Co(PMe_3)$(2,2′-biphenyl) (9)

	3	4	9
		Crystal Parameters	
chemical formula	$C_{32}H_{38}Rh_2$	$C_{32}H_{38}Co_2$	$C_{25}H_{32}CoP\cdot{}^1/_2$ hexane
formula weight	628.5	540.5	465.49
cryst syst	monoclinic	monoclinic	monoclinic
space group (No.)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
Z	8	8	4
a, Å	17.519(7)	19.8460(2)	8.688(2)
b, Å	16.018(8)	14.9123(2)	8.8350(12)
c, Å	20.738(15)	18.2262(3)	32.529(5)
β, deg	112.55(5)	103.86(0)	97.180(9)
vol, Å^3	5374.7(10.6)	5240.0(1)	2477.3(7)
ρ_{calcd}, g cm^{-3}	1.56	1.37	1.25
cryst dimens, mm	0.11 × 0.10 × 0.06	0.15 × 0.15 × 0.15	0.26 × 0.30 × 0.38
temp, °C	22	−50	−80
		Measurement of Intensity Data	
diffractometer	Enraf-Nonius CAD4	Siemens SMART	Siemens SMART
radiation	Mo Kα, 0.710 73	Mo Kα, 0.710 73	Mo Kα, 0.710 73
2θ range, deg	4−44	0−50	4−56.5
data collected	$+h,+k,\pm l$	$-25 \le h \le 26, -16 \le k \le 19, -16 \le l \le 24$	$-7 \le h \le 11, -11 \le k \le 10, -31 \le l \le 43$
no. of data collected	7135	25 495	14 811
no. of unique data	6874	8921	5702
agreement between equiv data	0.044	0.039	0.025
no. of observed data	4300 ($I > 2\sigma(I)$)	8921 ($I > 3\sigma(I)$)	984 ($I > 2\sigma(I)$)
no. of params varied	613	633	256
μ, cm^{-1}	12.43	12.84	7.70
abs corr	empirical (DIFABS)	differential (SADABS)	empirical (SADABS)
range of transmission factors	0.744−1.00	0.78−0.93	0.697−0.928
$R1(F_o)$, $wR2(F_o^2)$, ($I > 2\sigma(I)$)		0.0416, 0.0734	0.0546, 0.1199
$R1(F_o)$, $wR2(F_o^2)$, all data		0.0640, 0.0802	0.0639, 0.1244
$R1(F_o)$, $Rw(F_o)$, ($I > 3\sigma(I)$)	0.0383, 0.0373		
goodness of fit	1.51	1.06	1.22

Table 2. Selected Bond Distances (Å) and Angles (deg) for $(C_5Me_5)_2Rh_2$(2,2′-biphenyl) (3) and $(C_5Me_5)_2Co_2$(2,2′-biphenyl) (4)

	M = Rh, **3**[a]		M = Co, **4**[a]	
	molecule A	molecule B	molecule A	molecule B
M1−M2	2.675(2)	2.684(2)	2.4874(5)	2.4792(6)
M1−C1	1.999(9)	1.991(8)	1.905(3)	1.902(3)
M1−C12	2.015(8)	2.006(8)	1.899(3)	1.902(3)
M2−C1	2.251(8)	2.253(8)	2.082(3)	2.087(3)
M2−C6	2.188(9)	2.221(9)	2.092(3)	2.087(3)
M2−C7	2.201(9)	2.217(8)	2.084(3)	2.092(3)
M2−C12	2.250(9)	2.245(8)	2.089(3)	2.088(3)
C1−C6	1.39(1)	1.44(1)	1.442(4)	1.432(4)
C6−C7	1.49(1)	1.46(1)	1.448(4)	1.451(4)
C7−C12	1.45(1)	1.43(1)	1.434(4)	1.437(4)
C1−M1−C12	79.4(3)	79.6(3)	83.47(13)	83.17(13)
M1−C1−C6	119.0(6)	117.6(6)	115.6(2)	115.9(2)
C1−C6−C7	113.0(8)	112.4(8)	111.7(3)	112.4(3)
C6−C7−C12	111.3(8)	112.7(7)	112.6(3)	111.6(3)
C7−C12−M1	117.1(6)	117.3(6)	115.6(2)	116.1(2)

[a] Two independent molecules (A and B) in the asymmetric unit.

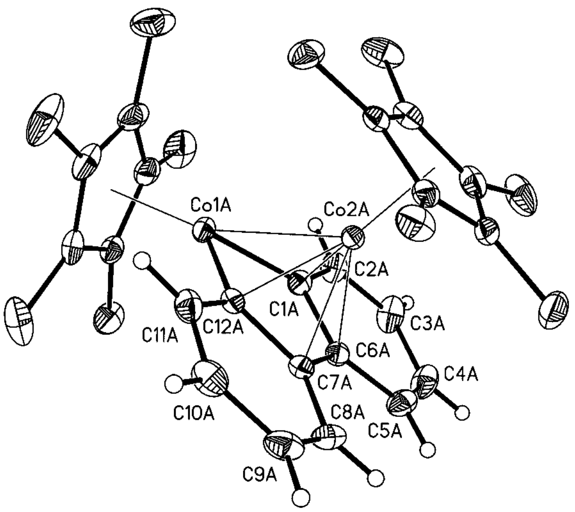


Figure 2. ORTEP drawing of $(C_5Me_5)_2Co_2$(2,2′-biphenyl) (**4**), showing the ellipsoids at the 30% probability level.

undergoing exchange. For $(C_5Me_5)_2Rh_2$(2,2′-biphenyl), coalescence of the two C_5Me_5 resonances was observed at 77 °C (350 K), corresponding to a rate of exchange of 290 s^{-1} and a $\Delta G^{\ddagger} = 16.8$ kcal/mol at that temperature.[12]

At room temperature, the ^1H NMR spectrum of $(C_5Me_5)_2Co_2$(2,2′-biphenyl) in THF-d_8 shows only one singlet for the $(C_5Me_5)Co$ fragments, which integrates for 30 H compared to the biphenyl resonances, indicative that the two ring environments are in rapid exchange. At low temperature, two distinct C_5Me_5 groups can be observed at δ 1.730 and 1.161 and coalescence to a singlet (δ 1.456) is observed at −25 °C (248 K). At that temperature, the rate of exchange is equal to 504 s^{-1} and $\Delta G^{\ddagger} = 11.4$ kcal/mol.[13]

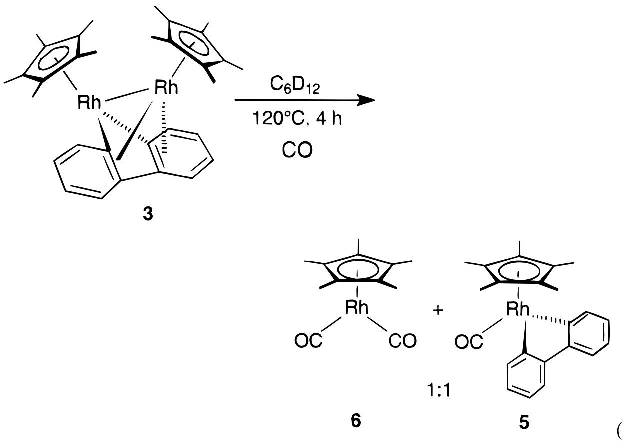
Reactivity of $(C_5Me_5)_2Rh_2$(2,2′-biphenyl). The reactivity of each dinuclear compound was investigated to determine if the $[(C_5Me_5)M]$ fragment binding to the two double bonds of the coordinated biphenyl ligand could be easily displaced by incoming ligands, thereby providing a pathway for further reactivity of the biphenyl ligand. An NMR sample of $(C_5Me_5)_2Rh_2$(2,2′-biphenyl) in c-C_6D_{12} was prepared and placed under 500 Torr of carbon monoxide. Upon heating to 120 °C, the solution was observed to gradually change color from dark purple to blue to green and finally to yellow after an hour. The complex was observed to have been

---

(12) Measurements were carried out on a Varian 200 MHz NMR spectrometer. At 25 °C (298 K), $\Delta\nu = 130.6$ Hz, $k_{350} = 2.22(\Delta\nu) = 290$ s^{-1}, $\Delta G^{\ddagger}$ (350 K) = 69.65 kJ/mol or 16.76 kcal/mol.

(13) At −60 °C (213 K), $\Delta\nu = 227.0$ Hz, $k_{248} = 2.22(\Delta\nu) = 504$ s^{-1}, $\Delta G^{\ddagger}$ (248 K) = 47.51 kJ/mol or 11.36 kcal/mol.

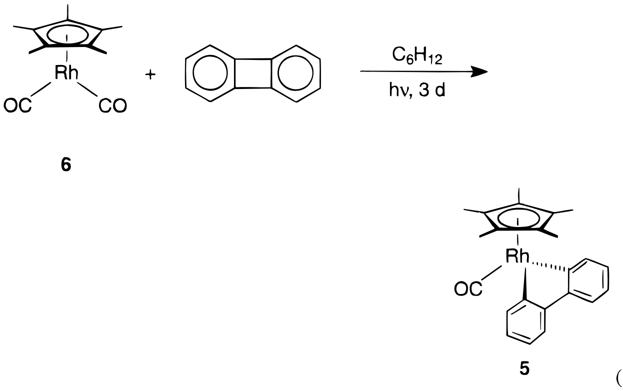
converted to a 1:1 mixture of two products by ^{1}H NMR spectroscopy (eq 3). One product was identified as the



(3)

dicarbonyl complex $(C_5Me_5)Rh(CO)_2$ (**6**) by comparison with an authentic sample;[14] the other compound was formulated as $(C_5Me_5)Rh(CO)(2,2'$-biphenyl) (**5**) based on its NMR data. The ^{1}H NMR spectrum exhibits the expected ABCD pattern for a coordinated biphenyl, and a ^{13}C-jmod spectrum revealed the presence of a quaternary carbon at δ 189.92 (d, $J = 77.8$ Hz), consistent with a terminal CO ligand.

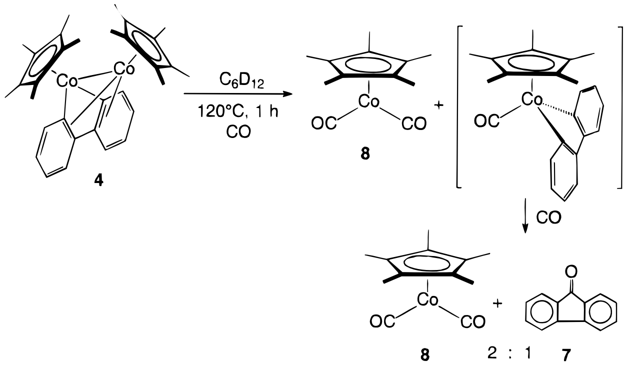
The "independent synthesis" of complex **5** was attempted by reaction of $(C_5Me_5)Rh(CO)_2$ with biphenylene. When carried out thermally, the reaction was unsuccessful; no reaction was observed at room temperature after 2 days and heating at elevated temperatures only resulted in decomposition of the dicarbonyl complex. Upon photolysis of a solution of complex **6** and biphenylene in cyclohexane, slow conversion of the dicarbonyl complex to **5** was observed and the reaction was complete after 3 days, with $(C_5Me_5)Rh(CO)(2,2'$-biphenyl) being the major organometallic species (eq 4).



(4)

5 presumably forms by the reaction of biphenylene with the photochemically formed fragment $[(C_5Me_5)Rh(CO)]$.[15] Two organic fragments, so far uncharacterized, were present in small quantities as well. Crystals of **5** were obtained from a hexane solution at −20 °C, but X-ray diffraction studies were unsuccessful.

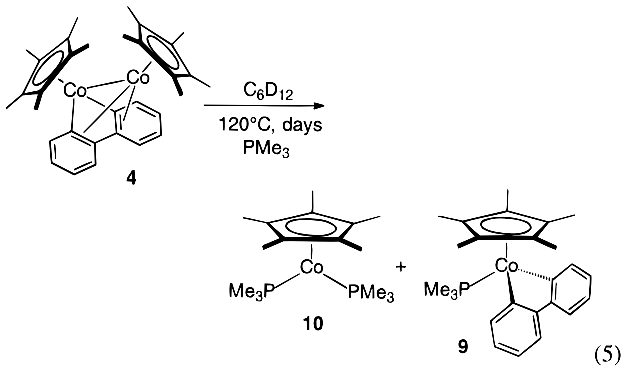
Scheme 2



The reactivity of $(C_5Me_5)_2Rh_2(2,2'$-biphenyl) with PMe_3 was also investigated. Surprisingly, complex **3** was found to be stable in the presence of 25 equiv of PMe_3, even at temperatures as high as 160 °C.

Reactivity of $(C_5Me_5)_2Co_2(2,2'$-biphenyl). $(C_5Me_5)_2Co_2(2,2'$-biphenyl) in cyclohexane-d_{12} solution was reacted with CO (500 Torr) at 120 °C. Over the course of 1 h, the black solution turned green and then yellow. The solution was shown to be a 1:2 mixture of fluorenone (**7**) and $(C_5Me_5)Co(CO)_2$ (**8**) by ^{1}H NMR spectroscopy, formed in quantitative yield. No starting material was left, and no intermediates of the type $(C_5Me_5)Co(CO)(2,2'$-biphenyl) could be detected, even though this complex is likely to be involved in the formation of fluorenone (Scheme 2). Complex **8** was characterized by comparison with an authentic sample.[16]

Unlike the rhodium analog, the cobalt complex was found to react slowly with excess PMe_3 to give a 2:1 mixture of $(C_5Me_5)Co(PMe_3)(2,2'$-biphenyl) (**9**) and $(C_5Me_5)Co(PMe_3)_2$ (**10**)[17] after several days at 120 °C (eq 5). Some decomposition was also observed. Complex **9** was isolated as extremely thin yellow plates from a hexane solution at −20 °C and was characterized by ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopies.



(5)

The solid state structure of **9** was also determined, and the molecule was found to crystallize in the monoclinic space group $P2_1/c$. The structure is very similar

---

[14] Prepared by the literature method, see: Kang, J. W.; Maitlis, P. M. *J. Organomet. Chem.* **1971**, *26*, 393−399.

[15] Rest, A. J.; Whitwell, I.; Graham, W. A. G.; Hoyano, J. K.; McMaster, A. D. *J. Chem. Soc., Chem. Commun.* **1984**, 624−626. Rest, A. J.; Whitwell, I.; Graham, W. A. G.; Hoyano, J. K.; McMaster, A. D. *J. Chem. Soc., Dalton Trans.* **1987**, 1181−1190. Weiller, B. H.; Wasserman, E. P.; Moore, C. B.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 4326−4330. Bromberg, S. E.; Lian, T.; Bergman, R. G.; Harris, C. B. *J. Am. Chem. Soc.* **1996**, *118*, 2069−2072.

[16] Frith, S. A.; Spencer, J. L. *Inorg. Synth.* **1990**, *28*, 273−274.

[17] Werner, H.; Heiser, B.; Klingert, B.; Dölfel, R. *J. Organomet. Chem.* **1982**, *240*, 179−190.

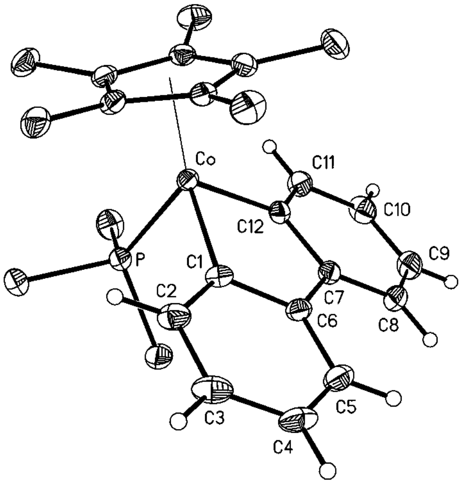


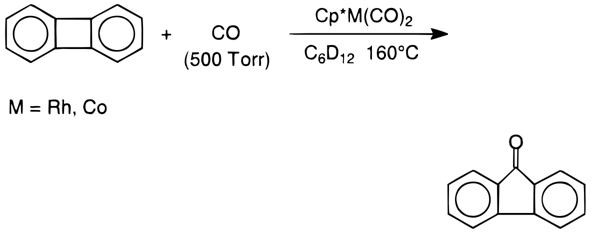
Figure 3. ORTEP drawing of $(C_5Me_5)Co(PMe_3)$(2,2′-biphenyl) (**9**), showing the ellipsoids at the 50% probability level. Selected bond distances (Å) and angles (deg): Co−C(1), 1.940(3); Co−C(12), 1.942(3); C(1)−C(6), 1.411(4); C(6)−C(7), 1.470(4); C(7)−C(12), 1.406(4); C(1)−Co−C(12), 83.48(12).

to the rhodium analog reported earlier.[6] One C−C bond has been cleaved to form a five-membered metallacycle, and the coordinated biphenyl is bent toward the PMe_3 group with the same 9.5° dihedral angle. An ORTEP drawing of **9** is shown in Figure 3, and Table 1 lists the data collection parameters.

Reaction of 3 and 4 with Hydrogen. Despite the reactivity with CO and PMe_3, both complexes **3** and **4** were found to be resistant to hydrogenation in cyclohexane-d_{12} under 500 Torr of hydrogen. Complex **3** was reacted at 170 °C for 10 h and complex **4** at 130 °C for 2 days. In both experiments, no significant change was observed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopies.

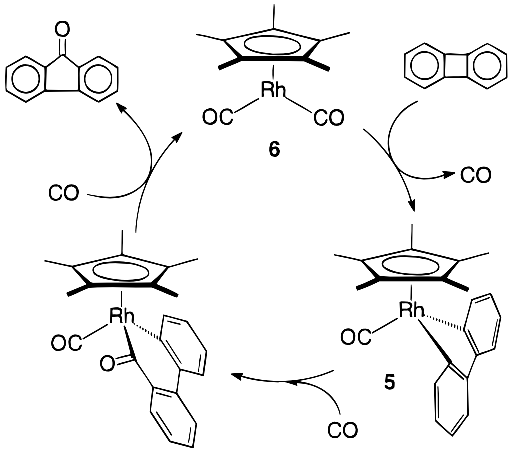
Catalytic Production of Fluorenone. When $(C_5Me_5)Rh(CO)_2$ was reacted with 4.5 equiv of biphenylene in the presence of CO in cyclohexane-d_{12}, no reaction was observed below 120 °C. At 160 °C, biphenylene was converted to fluorenone and no other species were seen besides $(C_5Me_5)Rh(CO)_2$. After 2 days, 55% of the substrate had been converted (~1 turnover/day), and the reaction went to completion in 6 days.

Similar results were obtained when the cobalt analog $(C_5Me_5)Co(CO)_2$ was used with 3 equiv of biphenylene. After 17 h at 170 °C, a 2:1 ratio of fluorenone to biphenylene was observed (3 turnovers/day) but decomposition of $(C_5Me_5)Co(CO)_2$ was observed in the form of a dark precipitate. Further heating brought the reaction to completion, but all $(C_5Me_5)Co(CO)_2$ had disappeared (eq 6). A control reaction demonstrated that biphenylene was unreactive under the same conditions of CO pressure in the absence of metal, even at 160 °C.



(6)

Scheme 3. Proposed Mechanism for the Catalytic Carbonylation of Biphenylene



The catalytic carbonylation of biphenylene to fluorenone seems more straightforward since the complex $(C_5Me_5)Rh(CO)$(2,2′-biphenyl) has been shown to eliminate fluorenone under the conditions of the catalytic reaction. Scheme 3 shows the proposed mechanism for the formation of fluorenone, where after loss of CO and formation of a C−C insertion adduct, the carbonyl ligand inserts into the M−C bond of the coordinated biphenyl. Displacement of fluorenone by CO gives back $(C_5Me_5)Rh(CO)_2$. The analogous Co complex probably follows the same pathway, but the intermediate $(C_5Me_5)Co(CO)$(2,2′-biphenyl) could not be observed.

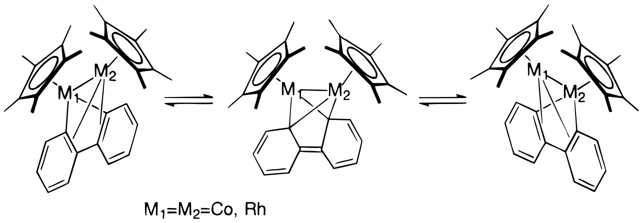
Discussion

The reaction to form $(C_5Me_5)_2Rh_2$(2,2′-biphenyl) is inhibited by the presence of ethylene in solution. As the reaction proceeds, the ethylene that is freed inhibits further reaction, consistent with a mechanism proceeding by elimination of ethylene prior to biphenylene activation. As the 16-electron fragment $[(C_5Me_5)Rh(C_2H_4)]$ is known to activate arene C−H bonds for H/D exchange, it is reasonable that such a species should also C−H activate biphenylene. Subsequent rearrangement to the C−C inserted product can then occur, as was observed previously with $(C_5Me_5)Rh(PMe_3)$(2-biphenylenyl)H.[6] The second ethylene ligand is likely to be labile in this Rh(III) adduct, and its loss leads to the formation of the isolated product **3**. A similar sequence of events leads to the formation of **4** from **2**.

Both complexes are fluxional and exchange the C_5Me_5 ring environments, with coalescence occurring at 77 °C for the rhodium complex and −25 °C for the cobalt complex (400 MHz) and activation barriers of 16.8 and 11.4 kcal/mol, respectively. This difference could be attributed to the M−C bond strength, the Co−C bond being slightly weaker than the Rh−C bond thus facilitating the exchange. A possible mechanism for this exchange is shown in Scheme 4, where the transition state/intermediate has both metal centers σ-bound to two quaternary carbons, thereby disrupting the aromaticity of the biphenyl ligand.

Binuclear complexes containing one metallacyclopentadiene unit η^5-bound to a second metal are well-documented in organometallic chemistry. Most of the

Scheme 4



complexes that have been characterized are static,[18] but a few are known to be fluxional[19] in the same fashion as **3** and **4**. Of interest to the current study, two dicobalt complexes have been reported with similar bridging moieties. One of these, CpCo(1−3,8,9-η-(1-Cp-3-Me-1-cobaltaindenyl)), is similar to **4** but with one of the benzene rings replaced by a β-methyl group.[20] Unlike **4**, the complex is static at room temperature, but no NMR data were reported at elevated temperatures. The analogous diiridium complex is also static.[21] Another similar dicobalt complex reported in the literature is [η^4-(CpCo−CR═CR−CR═CR)](CoCp) (where R = Cl), which is also is static at room temperature by ^1H and ^{13}C NMR spectroscopies.[22] By comparison, the related complex with R = H was found to be fluxional, with $\Delta G^{\ddagger}$ (248 K) = 23.7 kcal/mol.[23] Replacement of the hydrogens by methyl groups also gives a fluxional complex, with $\Delta G^{\ddagger}$ = 19.2 kcal/mol.[24] Complexes **3** and **4** both display lower fluxional barriers, which can be attributed to the fact that the η^4-bonding is to the double bonds of aromatic rings in a biphenyl system.

The difference in reactivity between **3** and **4** with small molecules is also consistent with a stronger Rh−C bond, as expected for a second-row transition metal compared to a first-row metal like Co. This difference explains the absence of reaction of **3** in the presence of PMe_3, while the cobalt analog slowly converts to $(C_5Me_5)Co(PMe_3)$(2,2′-biphenyl) and $(C_5Me_5)Co(PMe_3)_2$. Similarly, the formation of fluorenone when **4** is reacted with CO while $(C_5Me_5)Rh(CO)$(2,2′-biphenyl) remains stable is accounted for by stronger Rh−C bonds vs Co−C bonds. More puzzling is the resistance of both species to hydrogenation. A steric effect can probably be ruled out since other ligands react. A more likely explanation is that CO and PMe_3 have the ability to act as σ-donors that can attack and cleave **3** and **4**. In addition, reaction of **3** and **4** with H_2 is likely to proceed by oxidative addition to the metal center, which would be difficult with the Rh(III) and Co(III) moieties.

Conclusion

The reactions of $(C_5Me_5)Rh(C_2H_4)_2$ and $(C_5Me_5)Co(C_2H_4)_2$ with biphenylene yield the same type of dinuclear product $(C_5Me_5)_2M_2$(2,2′-biphenyl) where a C−C bond of biphenylene has been activated. A fluxional process exchanges the C_5Me_5 rings by interchanging σ- and π-bonding of the biphenyl ligand. Both complexes are resistant to hydrogenation but react with carbon monoxide to form the dicarbonyl complex $(C_5Me_5)M(CO)_2$ and fluorenone or $(C_5Me_5)Rh(CO)$(2,2′-biphenyl) for cobalt and rhodium, respectively. Complex **4** reacts with PMe_3 to give a mixture of $(C_5Me_5)Co(PMe_3)$(2,2′-biphenyl) and $(C_5Me_5)Co(PMe_3)_2$, while **3** is found to be unreactive, reflecting the presence of a stronger Rh−C bond.

Experimental Section

General Considerations. All manipulations were done under nitrogen unless otherwise specified, either in a Vacuum Atmospheres Corp. glovebox or on a high-vacuum line using modified Schlenk techniques. All solvents were distilled from benzophenone ketyl solution under nitrogen. Olefin-free hexanes and cyclohexane were obtained by treatment with sulfuric acid before drying. Deuterated solvents were dried before use and kept in Teflon-sealed ampules. Cyclohexane-d_{12} and *n*-hexane-d_{18} were purchased from Cambridge Isotope Lab. NMR spectra were recorded on a Bruker AMX-400 spectrometer; all chemical shifts are reported in ppm (δ) relative to tetramethysilane and referenced to the chemical shift of residual solvent resonances (C_6D_6, 7.15; *c*-C_6D_{12}, 1.38; *n*-C_8D_{18}, 0.83 and 1.24). The chemical shifts of the ^{31}P NMR spectra are reported in units of δ (ppm) relative to 30% H_3PO_4. The chemical shift of the ^{13}C NMR spectra is reported in units of δ (ppm) relative to tetramethylsilane, using the solvent peak as an internal reference (C_6D_6, 128.0; *c*-C_6D_{12}, 26.4; *n*-C_8D_{18}, 13.7, 22.9, 29.7, 32.2). Biphenylene and PMe_3 were purchased from Aldrich and used without further purification. Carbon monoxide was purchased from Air Products and was either of technical or CP grade. $(C_5Me_5)Rh(C_2H_4)_2$,[9] $(C_5Me_5)Co(C_2H_4)_2$,[10] $(C_5Me_5)Rh(CO)_2$,[14] and $(C_5Me_5)Co(CO)_2$[16] were prepared by literature methods. Photolysis was done using an Oriel Corp. UV Lamp model 6137. Analyses were obtained from Desert Analytics.

Synthesis of $(C_5Me_5)_2Rh_2$(2,2′-biphenyl). A 150 mg (0.51 mmol) amount of yellow $(C_5Me_5)Rh(C_2H_4)_2$ and 40 mg (0.26 mmol, 0.5 equiv) of biphenylene were mixed in a Teflon-sealed ampule and dissolved in 15 mL of dry, olefin-free cyclohexane. The solution was degassed by three freeze−pump−thaw cycles and heated at 120 °C for 24 h. The reaction mixture was allowed to cool, and most of the ethylene was removed under vacuum along with approximately 1 mL of solvent. The reaction mixture was heated for an additional 36 h at 120 °C, allowed to cool, and concentrated to 5 mL by removal of the solvent under vacuum. Hexane (1 mL) was added, and the solution was left to recrystallize at −20 °C. Dark purple crystals of $(C_5Me_5)_2Rh_2$(2,2′-biphenyl) (**3**) were obtained in a few days (83% yield). Anal. Calcd (found) for $Rh_2C_{32}H_{38}$: C, 61.16 (61.18); H, 6.09 (6.05). ^1H NMR (*c*-C_6D_{12}): δ 1.240 (s, 15 H), 1.892 (s, 15 H), 6.681 (dd, J = 6.7, 8.5 Hz, 2 H), 6.988 (dd, J = 6.7, 8.6 Hz, 2 H), 7.426 (d, J = 8.6 Hz, 2 H), 7.501 (d, J = 8.5 Hz, 2 H). ^1H NMR (*n*-C_8D_{18}): δ 1.245 (s, 15 H), 1.896 (s, 15 H), 6.697 (t, J = 7.4 Hz, 2 H), 7.006 (t, J = 8.0 Hz, 2 H), 7.441 (d, J = 8.7 Hz, 2 H), 7.512 (d, J = 8.5 Hz, 2 H). $^{13}C\{^1H\}$ NMR (*n*-C_8D_{18}): δ 8.76 (s, C_5*Me*$_5$), 11.41 (s, C_5*Me*$_5$), 91.34 (d, J = 7.6 Hz, *C*$_5$Me$_5$), 93.66 (d, J = 5.1 Hz, *C*$_5$Me$_5$), 113.21 (s,

---

(18) For example, see: Connelly, N. G.; Excher, T.; Martín, A. J.; Metz, B.; Orpen, A. G. *J. Cluster Sci.* **1995**, *6*, 125−134. Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6806−6815. Knox, S. A. R.; Stansfield, R. F. D.; Stone, F. G. A.; Winter, M. J.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1982**, 173−185. Daran, J.-C.; Jeannin, Y. *Organometallics* **1984**, *3*, 1158−1163. Daran, J.-C.; Gilbert, E.; Gouygou, M.; Halut, S.; Heim, B.; Jeannin, Y. *J. Cluster Sci.* **1994**, *5*, 373−400. Müller, J.; Schubert, R.; Tschampel, M.; Pickardt, J. *J. Organomet. Chem.* **1995**, *502*, 53−60.

(19) Veldman, M. E. E.; Van der Wal, H. R.; Veenstra, S. J.; de Liefde Meijer, H. J. *J. Organomet. Chem.* **1980**, *197*, 59−65. Bonrath, W.; Michaelis, S.; Pörschke, K. R.; Gabor, B.; Mynott, R.; Krüger, C. *J. Organomet. Chem.* **1990**, *397*, 255−260. Michaelis, S.; Pörschke, K.; Mynott, R.; Goddard, R.; Krüger, C. *J. Organomet. Chem.* **1992**, *426*, 131−141.

(20) Wadepohl, H.; Borchert, T.; Büchner, K.; Herrmann, M.; Paffen, F.-J.; Pritzkow, H. *Organometallics* **1995**, *14*, 3817−3826.

(21) McGhee, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 4246−4262.

(22) Sünkel, K. *J. Organomet. Chem.***1990**, *391*, 247−257.

(23) Rosenblum, M.; North, B.; Wells, D.; Giering, W. P. *J. Am. Chem. Soc.* **1972**, *94*, 1239−1246.

(24) Lee, W.-S.; Brintzinger, H. H. *J. Organomet. Chem.***1977**, *127*, 93−103.

quat C), 121.12 (s), 122.95 (s), 125.15 (s), 145.13 (s), 149.27 (dd, $J_{\mathrm{C-Rh_1}} = 44.8$ Hz, $J_{\mathrm{C-Rh_2}} = 14.8$ Hz).

X-ray Structural Determination of $(C_5Me_5)_2Rh_2$(2,2′-biphenyl). A dark red crystal was obtained from an *n*-octane-d_{18} solution at room temperature and mounted with epoxy on a glass fiber. A primitive monoclinic lattice was found using 25 reflections with values of χ between 0 and 70°. Collection of one quadrant of data was undertaken at −20 °C and was followed by data reduction using the Molecular Structure Corp. TEXSAN analysis software package.[25] The rhodium atoms (2 molecules/asymmetric unit) were located with the program MITHRIL, and all non-hydrogen atoms were revealed by expansion of the structure with the program DIRDIF. Isotropic refinement and absorption corrections (DIFABS) were performed, and full-matrix least-square anisotropic refinement of the non-hydrogen atoms with hydrogens attached to carbons in idealized positions was carried out to convergence. Data collection parameters are given in Table 1, selected distances and angles are listed in Table 2. All bond distances and angles and positional and thermal parameters are available in the Supporting Information.

Synthesis of $(C_5Me_5)_2Co_2$(2,2′-biphenyl). A 15 mg amount of red $(C_5Me_5)Co(C_2H_4)_2$ (0.03 mmol) and 4 mg (0.03 mmol, 1 equiv) of biphenylene were placed in a resealable NMR tube, and 0.5 mL of *c*-C_6D_{12} was vacuum-distilled into it. The NMR tube was heated at 90 °C in an oil bath for 4 days, resulting in quantitative conversion of the starting material to the new product $(C_5Me_5)_2Co_2$(2,2′-biphenyl) (**4**). Slow evaporation of the solution gave black needle-like crystals of **4** (75% yield). ^{1}H NMR (*c*-C_6D_{12}): δ 1.436 (s, 30 H), 7.003 (t, $J = 7.1$ Hz, 2 H), 7.138 (t, $J = 7.3$ Hz, 2 H), 7.469 (d, $J = 8.5$ Hz, 2 H), 8.357 (d, $J = 8.4$ Hz, 2 H). $^{13}C\{^1H\}$ NMR (*c*-C_6D_{12}): δ 9.98 (s, $C_5\mathit{Me}_5$), 86.57 (s, C_5Me_5), 116.35 (s, quat C), 122.35 (s), 122.93 (s), 127.44 (s), 144.20 (s, quat C), 150.41 (s). Anal. Calcd (found) for $C_{34}H_{38}Co_2$: C, 71.11 (71.33); H, 7.09 (6.85). MS: *m/e* 540 (M^+).

X-ray Structural Determination of $(C_5Me_5)_2Co_2$(2,2′-biphenyl). Dark black prisms were obtained by slow evaporation of a hexane solution of **4**. A single crystal having approximate dimensions of 0.15 × 0.15 × 0.15 mm^3 was mounted on a glass fiber with epoxy. Data were collected at −50 °C on a Siemens SMART CCD area detector system employing a 3 kW sealed tube X-ray source operating at 1.5 kW. Data (1.3 hemispheres) were collected over 7 h (10 s frames), yielding 25 495 observed data after integration using SAINT (see Table 1). Laue symmetry revealed a monoclinic crystal system, and cell parameters were determined from 6565 unique reflections.[26] The space group was assigned as $P2_1/c$ on the basis of systematic absences using XPREP, and the structure was solved and refined using SHELX95. For a Z value of 8, there are two independent molecules within the asymmetric unit. In the final model, non-hydrogen atoms were refined anisotropically (on F^2), with hydrogens included in idealized locations. The structure was refined with $R1 = 0.0416$ and $wR2 = 0.0734$.[27] Fractional coordinates, thermal parameters, and a complete listing of distances and angles are given in the Supporting Information.

Reaction of $(C_5Me_5)_2Rh_2$(2,2′-biphenyl) with CO. An NMR sample of $(C_5Me_5)_2Rh_2$(2,2′-biphenyl) in *c*-C_6D_{12} was prepared, and 500 Torr of CO was added *via* the vacuum line. Upon heating at 120 °C, the dark purple solution rapidly turned blue then green and finally yellow in 1 h. Heating for an additional 3 h did not result in any color change. The mixture was characterized by ^{1}H and ^{13}C NMR as a 1:1 mixture of $(C_5Me_5)Rh(CO)$(2,2′-biphenyl) (**5**) and $(C_5Me_5)Rh(CO)_2$ (**6**) (quantitative yield by NMR). ^{1}H NMR for **5** (*c*-C_6D_{12}): δ 1.738 (s, 15 H), 6.825 (td, $J = 7.4$, 1.5 Hz, 2 H), 6.955 (td, $J = 7.4$, 1.1 Hz, 2 H), 7.334 (d, $J = 7.5$ Hz, 2 H), 7.389 (dd, $J = 7.6$, 1.4 Hz, 2 H). $^{13}C\{^1H\}$ NMR for **5** (*c*-C_6D_{12}): δ 9.83 (s, $C_5\mathit{Me}_5$), 102.87 (d, $J = 3.6$ Hz, C_5Me_5), 121.76 (s), 124.85 (s), 126.34 (s), 137.60 (s), 154.45 (s, quat C), 162.60 (d, $J_{\mathrm{RhC}} = 32.1$ Hz, quat C), 189.92 (d, $J_{\mathrm{RhC}} = 77.8$ Hz, CO). ^{1}H NMR for **6** (*c*-C_6D_{12}): δ 2.000 (s, 15 H). $^{13}C\{^1H\}$ NMR for **6** (*c*-C_6D_{12}): δ 11.05 (s, $C_5\mathit{Me}_5$), 100.99 (d, $J = 4.1$ Hz, C_5Me_5), 194.31 (d, $J = 83.9$ Hz, CO).

Photolysis of $(C_5Me_5)Rh(CO)_2$ in the Presence of Biphenylene. A 5 mg (0.017 mmol) amount of $(C_5Me_5)Rh(CO)_2$ (**6**) was placed in a resealable NMR tube with 10 mg (0.07 mmol, 4 equiv) of biphenylene and dissolved in 0.5 mL of dry, olefin-free cyclohexane. Photolysis was carried out for 3 days, the volatiles were removed under vacuum, and 0.5 mL of cyclohexane-d_{12} was vacuum-distilled into the NMR tube. Complex **5** was found to be the major organometallic species, but other C_5Me_5 resonances could be detected as well. Removal of the solvent under vacuum and extraction with 0.5 mL of hexane yielded a red solution, from which some crystals of **5** could be obtained by recrystallization at −20 °C. A white solid was left behind, and the ^{1}H NMR spectrum in C_6D_6 revealed two organic species (**7a**,**b**). These species were not identified, but their ^{1}H NMR data do not match the resonances for tetraphenylene, triphenylene, fluorenone, or anthroquinone. ^{1}H NMR for **7a** (C_6D_6): δ 5.552 (dd, $J = 9.7$, 3.1 Hz, 4 H), 6.225 (dd, $J = 9.3$, 2.8 Hz, 4 H). ^{1}H NMR for **7b** (C_6D_6): δ 6.861 (dd, $J = 5.6$, 3.3 Hz, 4 H), 7.047 (dd, $J = 5.6$, 3.3 Hz, 4 H).

Reaction of $(C_5Me_5)_2M_2$(2,2′-biphenyl) with H_2 (M = Rh, Co). Both experiments were carried out in similar ways by dissolving about 5 mg of $(C_5Me_5)_2M_2$(2,2′-biphenyl) in 0.5 mL of *c*-C_6D_{12} in a resealable NMR tube. Hydrogen (500 Torr) was then added to the sample *via* the vacuum line, and the NMR tube was heated at 130 °C for 2 days for the cobalt complex and at 170 °C for 10 h for the rhodium analog. No change could be detected in the solution by ^{1}H NMR spectroscopy in either experiment.

Reaction of $(C_5Me_5)_2Co_2$(2,2′-biphenyl) with CO. A sample of $(C_5Me_5)_2Co_2$(2,2′-biphenyl) (∼3 mg) in *c*-C_6D_{12} was prepared in a resealable NMR tube, and 500 Torr of CO was added *via* the vacuum line. The NMR tube was heated at 120 °C in an oil bath; the black solution turned green in 15 min and was yellow after 1 h. ^{1}H NMR spectroscopy revealed that the mixture was composed of 1 equiv of fluorenone (**7**) and 2 equiv of $(C_5Me_5)Co(CO)_2$ (**8**) and no other observed species. ^{1}H NMR for **7** (*c*-C_6D_{12}): δ 7.165 (t, $J = 7.3$ Hz, 2 H), 7.326 (t, $J = 7.3$ Hz, 2 H), 7.402 (d, $J = 7.5$ Hz, 2 H), 7.559 (d, $J = 7.3$ Hz, 2 H). ^{1}H NMR for **8** (*c*-C_6D_{12}): δ 1.860 (s, 15 H).

Reaction of $(C_5Me_5)_2Co_2$(2,2′-biphenyl) with PMe_3. A sample containing 10 mg (0.016 mmol) of $(C_5Me_5)_2Co_2$(2,2′-biphenyl) in *c*-C_6D_{12} was prepared in a resealable NMR tube. Three equivalents of PMe_3 was added, the tube was heated at 120 °C in an oil bath, and the reaction was monitored by ^{1}H and $^{31}P\{^1H\}$ NMR spectroscopy. The starting material was slowly converted to a mixture of $(C_5Me_5)Co(PMe_3)$(2,2′-biphenyl) (**9**) and $(C_5Me_5)Co(PMe_3)_2$ (**10**). After 5 days, only 43% of **4** had reacted. PMe_3 (2 equiv) was added to the reaction mixture *via* the vacuum line, and the sample was heated for an additional 4.5 days. By ^{1}H and $^{31}P\{^1H\}$ NMR spectroscopy, all of the starting material was found to have been converted to a 2:1 mixture of **9** and **10** (95% NMR yield). ^{1}H NMR for **9** (*c*-C_6D_{12}): δ 0.732 (d, $J = 9.4$ Hz, 9 H), 1.496 (s, 15 H), 6.769 (t, $J = 7.3$ Hz, 2 H), 6.853 (t, $J = 7.3$ Hz, 2 H), 7.332 (d, $J = 7.6$ Hz, 2 H), 7.413 (d, $J = 7.0$ Hz, 2 H). $^{31}P\{^1H\}$ NMR for **9** (*c*-C_6D_{12}): δ 27.6 (br s). $^{13}C\{^1H\}$ NMR for **9** (*c*-C_6D_{12}): δ 10.31

---

(25) $R_1 = \{\sum||F_o| - |F_c||\}/\{\sum|F_o|\}$; $R_2 = \{\sum w(|F_o| - |F_c|)^2\}^{1/2}/\{\sum wF_o^2\}$, 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.

(26) It has been noted that the integration program SAINT produces cell constant errors that are unreasonably small, since systematic error is not included. More reasonable errors might be estimated at 10× the listed values.

(27) Using the SHELX95 package, $R1 = (\sum||F_o| - |F_c||)/\sum|F_o|$, $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]\}^{1/2}$, where $w = 1/[\sigma 2(F_o^2) + (a\cdot P)^2 + b\cdot P]$ and $P = [f\cdot(\text{maximum of 0 or } F_o^2) + (1 - f)\cdot F_c^2]$.

(s, C_5*Me*$_5$), 14.92 (d, J = 30.0 Hz, PMe_3), 94.85 (s, *C*$_5$Me$_5$), 120.51 (d, J = 3.6 Hz), 122.82 (s), 126.38 (s), 138.36 (d, J = 3.6 Hz), 156.56 (d, J = 4.1 Hz, quat C), the other quaternary carbon could not be detected.

X-ray Structural Determination of $(C_5Me_5)Co(PMe_3)$-(2,2′-biphenyl). Yellow plates of $(C_5Me_5)Co(PMe_3)$(2,2′-biphenyl) were obtained from a hexane solution at −20 °C. A single crystal having approximate dimensions of 0.26 × 0.30 × 0.38 mm^3 was mounted on a glass fiber with epoxy. Data were collected at −80 °C on a Siemens SMART CCD area detector system employing a 3 kW sealed tube X-ray source operating at 1.5 kW. Data (1.3 hemispheres) were collected over 7 h (10 s frames), yielding 14 811 observed data after integration using SAINT (see Table 1). Laue symmetry revealed a monoclinic crystal system, and cell parameters were determined from 8192 unique reflections.[26] The space group was assigned as $P2_1/c$ on the basis of systematic absences using XPREP, and the structure was solved and refined using SHELX95. For a Z value of 4, there is one independent molecule within the asymmetric unit. In the final model, non-hydrogen atoms were refined anisotropically (on F^2), with hydrogens included in idealized locations. The structure was refined with R1 = 0.0546 and wR2 = 0.1199.[27] Data collection parameters are given in Table 1. Bond distances and angles and thermal and positional parameters are given in the Supporting Information.

Carbonylation of Biphenylene with $(C_5Me_5)Rh(CO)_2$. In a resealable NMR tube were mixed 4 mg (0.014 mmol) of $(C_5Me_5)Rh(CO)_2$ and 10 mg (0.06 mmol, 4.5 equiv) of biphenylene. *c*-C_6D_{12} (0.5 mL) was vacuumed-distilled into the tube and sealed under 500 Torr of CO. The NMR tube was heated at 160 °C in an oil bath, and the reaction was followed by ^{1}H NMR spectroscopy. After 48 h, 55% of the starting biphenylene had been converted to fluorenone, and the reaction was almost complete after 6 days. No species other than (C_5Me_5)-$Rh(CO)_2$, fluorenone (96.7%), and some unreacted biphenylene (3.3%) could be detected. NMR data for fluorenone: ^{1}H NMR (*c*-C_6D_{12}) δ 7.165 (t, J = 7.3 Hz, 2 H), 7.326 (t, J = 7.3 Hz, 2 H), 7.402 (d, J = 7.5 Hz, 2 H), 7.559 (d, J = 7.3 Hz, 2 H).

Carbonylation of Biphenylene with $(C_5Me_5)Co(CO)_2$. An NMR sample was prepared as described above, with 5 mg (0.02 mmol) of $(C_5Me_5)Co(CO)_2$ and 10 mg (0.06 mmol, 3 equiv) of biphenylene. The reaction was carried out at 170 °C and monitored by ^{1}H NMR spectroscopy. After 17 h, the orange solution had turned green and reverted to yellow upon cooling. The ^{1}H NMR spectrum revealed that 66% of the starting material had reacted to give fluorenone. The resonance for $(C_5Me_5)Co(CO)_2$ was observed to decrease, consistent with decomposition seen in the form of a black solid on the walls of the tube. After 45 h, all of the biphenylene was consumed and fluorenone was observed as the major product (85% yield), but 90% of the $(C_5Me_5)Co(CO)_2$ had decomposed.

Acknowledgment is made to the U.S. Department of Energy Office of Basic Energy Sciences (FG02-86ER13569) for their support of this work. We also thank Dr. Rene Lachicotte for assistance with the structure of **9**.

Supporting Information Available: Tables of data collection parameters, all bond distances and angles, fractional atomic coordinates, anisotropic thermal parameters, and hydrogen atom coordinates for $(C_5Me_5)_2Rh_2$(2,2′-biphenyl) (**3**), $(C_5Me_5)_2Co_2$(2,2′-biphenyl) (**4**), and $(C_5Me_5)Co(PMe_3)$(2,2′-biphenyl) (**9**) (28 pages). Ordering information is given on any current masthead page.

OM961059A