(3) Where L_2 has the conformationally rigid 1,10-phenanthroline skeleton, hydrogen transfer—plausibly reductive C–H elimination—contributes substantially to rate control.

(4) Where L is PEt_3, Pt–P dissociation is a prerequisite, but not the rate-limiting, process. Reductive C–H elimination, again, plausibly makes the most energetic contribution to rate control.

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Synthesis, Oxidative Addition, and Structural Studies of the Metal–Metal Bonded Bimetallic Complexes $[(\eta^5\text{-}C_5H_5)Rh(\mu\text{-}CO)(\mu\text{-}Ph_2PC_5H_4N)M(CO)Cl]$ (M = Rh, Ir)

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Reaction of $[Rh(\eta^5\text{-}C_5H_5)(CO)_2]$ or $[Rh_2(\eta^5\text{-}C_5H_5)_2(CO)_3]$ with 2-(diphenylphosphino)pyridine (Ph_2PPy) gave $[Rh(\eta^5\text{-}C_5H_5)(CO)(Ph_2PPy)]$ (1) in which Ph_2PPy acts as monodentate P-bonded ligand. Compound 1 reacted with $[Rh(CO)_2Cl]_2$ and $[Ir(CO)_2(p\text{-toluidine})Cl]$ to give the Ph_2PPy-bridged complexes $[(\eta^5\text{-}C_5H_5)Rh(\mu\text{-}CO)(\mu\text{-}Ph_2PPy)Rh(CO)Cl]$ (2) and $[(\eta^5\text{-}C_5H_5)Rh(\mu\text{-}CO)(\mu\text{-}Ph_2PPy)Ir(CO)Cl]$ (3), respectively, in which a metal–metal bond is present. The structure of the unsymmetrical bimetallic compound 2 has been determined by X-ray crystallography. The crystal is monoclinic with space group $P2_1/c$, and the cell constants are $a = 15.928$ (2) Å, $b = 11.322$ (2) Å, $c = 26.646$ (4) Å, $\beta = 104.2$ (2)°, and $Z = 8$. The structure has been refined to a final R value of 0.042. The unit cell contains two crystallographically independent molecules that have very similar structures. The structure is characterized by the short Rh(1)–Rh(2) bond distance of 2.648 (1) Å, by the different coordination geometry of the two rhodium atoms, and by the presence of an asymmetric CO bridging ligand. The ligands about Rh(1) are disposed in an approximately tetrahedral environment, and the Rh(2) coordination geometry is that of a distorted square pyramid with the vertex shifted toward the Rh(1)–Rh(2) vector. The Ph_2PPy is twisted about the Rh(1)–Rh(2) bond to avoid unfavorable contacts. 2 reacts with SO_2 to produce $[(\eta^5\text{-}C_5H_5)Rh(\mu\text{-}Ph_2PPy)(\mu\text{-}SO_2)Rh(CO)Cl]$ (4). The addition of Cl_2 or Br_2 to 2 gave the rhodium(III) complexes $[(\eta^5\text{-}C_5H_5)X_2Rh(\mu\text{-}Ph_2PPy)Rh(CO)X_3]$ (5, X = Cl; 6, X = Br); the same reaction with I_2 occurred with formation of $[(\eta^5\text{-}C_5H_5)Rh(\mu\text{-}I)(\mu\text{-}Ph_2PPy)Rh(CO)I_2]$ (7) and $[(\eta^5\text{-}C_5H_5)I_2Rh(\mu\text{-}Ph_2PPy)Rh(CO)I_3]$ (8). Spectroscopic data indicated that 7 is a Rh^{II}–Rh^{II} species. It crystallizes in the monoclinic system, space group $P2_1/c$, with $a = 7.847$ (1) Å, $b = 16.995$ (2) Å, $c = 19.446$ (3) Å, $\beta = 96.4$ (1)°, and $Z = 4$. The structure has been refined to a final R value of 0.026. The rhodium atoms are bridged by the Ph_2PPy and I(1) ligands. The Rh(1)–Rh(2) bond distance of 2.686 (1) Å is very close to that of the precursor 2. The bond angles at Rh(1) atom reflect a large deviation from the tetrahedral coordination geometry. The Rh(2) atom displays a distorted octahedral geometry; significant deviations are with the terminal I(3) and bridging I(1) atoms. The geometry of the bridging iodo ligand appears normal. The structural features of the bridging Ph_2PPy and of the cyclopentadienyl ring are essentially the same as in the precursor 2. Compounds 7 and 8 have been the only products obtained from the reaction of 2 with CH_2I_2.

Introduction

In recent years there has been considerable interest in the synthesis, structural characterization, and reactivity of binuclear complexes in which two metals are held in close proximity by bridging ligands.[1,2] Interest in such bimetallic systems rises from their potential to activate small molecules through cooperative interactions with the metal centers and to act as homogeneous catalysts.[1-3]

Although there are exceptions,[4] bridging ligands such as bis(diphenylphosphino)methane[1,2] (dppm), bis(diphenylarsino)methane[5] (dpam), 2-(diphenylphosphino)-

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pyridine[6] (Ph_2PPy), phosphido,[7] and thiolato[8] groups have been found to preserve the binuclear framework during chemical transformations.

Previously we have reported the dirhodium η^5-cyclopentadienyl complex $[Rh_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-dppm})]$,[9] which is characterized by an electron-rich rhodium–rhodium bond. This bond easily adds metal electrophiles such as AgY (Y = CF_3COO, CH_3COO, PF_2O_2, $(C_2H_5)_2NCS_2$), $Ag_2CH_2(COO)_2$, CuX (X = Cl, I), $[AuPPh_3]^+$, and $HgCl_2$ giving triangular mixed-metal clusters.[10-14] In contrast, it shows little reactivity with acetylenes and alkyl halides, which are known to add across metal–metal bonds in bimetallic compounds containing the metal centers in low oxidation state.

In order to make the rhodium–rhodium bond unsymmetric, we wished to replace dppm by the Ph_2PPy ligand. The introduction of polarity into the rhodium–rhodium bond should increase its reactivity, especially toward polar reagents. However, unlike dppm,[9] Ph_2PPy reacts with $[Rh(\eta^5\text{-}C_5H_5)(CO)_2]$ or $[Rh_2(\eta^5\text{-}C_5H_5)_2(CO)_3]$, giving the mononuclear complex $[Rh(\eta^5\text{-}C_5H_5)(CO)(Ph_2PPy)]$ (1). We have used this complex as the starting material for the synthesis of 2-(diphenylphosphino)pyridine-bridged unsymmetric dirhodium(I) and heterobimetallic rhodium(I)–iridium(I) complexes in which the two metal atoms are in the same oxidation state but with different coordination number. Complexes of this type were expected to exhibit considerable reactivity, especially toward small unsaturated molecules. In this paper we report the results of this investigation together with the X-ray structures of the dirhodium(I) complex $[(\eta^5\text{-}C_5H_5)Rh(\mu\text{-}CO)(\mu\text{-}Ph_2PPy)Rh(CO)Cl]$ (2) and of its iodine oxidative addition product $[(\eta^5\text{-}C_5H_5)Rh(\mu\text{-}I)(\mu\text{-}Ph_2PPy)Rh(CO)I_2]$ (7).

Results and Discussion

Synthesis and Characterization. Treatment of $[Rh(\eta^5\text{-}C_5H_5)(CO)_2]$ or $[Rh(\eta^5\text{-}C_5H_5)_2(CO)_3]$ with Ph_2PPy in refluxing heptane yielded an orange solution from which orange crystals of $[Rh(\eta^5\text{-}C_5H_5)(CO)(Ph_2PPy)]$ (1) were obtained in high yield after purification by column chromatography. By monitoring the IR spectra during the reaction, we observed the progressive disappearance of the ν(CO) bands of the starting material together with the appearance of a new ν(CO) band, indicating that 1 was the only product. Besides the absorptions of the cyclopentadienyl and of coordinated Ph_2PPy, the IR spectrum of 1 showed only a single terminal ν(CO) band. In the ^1H NMR spectrum (CD_2Cl_2) the resonance of the cyclopentadienyl protons appears as a triplet at δ 5.18 [$^3J(^{31}P-^1H) = {}^2J(^{103}Rh-^1H) = 0.6$ Hz], while the $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$) showed a doublet at δ 53.8 [$^1J(^{103}Rh-^{31}P) = 199.8$ Hz], as expected for a structure in which a tertiary phosphorus atom is directly bonded to a rhodium(I) center.[15]

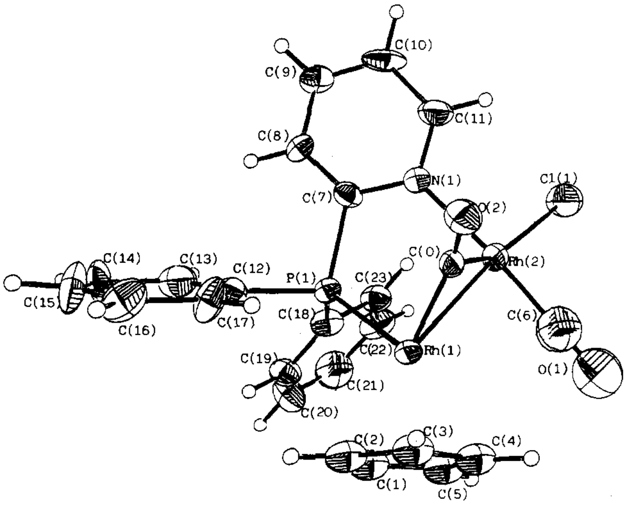

Figure 1. View of the molecule $[(\eta^5\text{-}C_5H_5)Rh(\mu\text{-}CO)(\mu\text{-}Ph_2PPy)Rh(CO)Cl]$.

Compound 1 can act as a monodentate metal-containing ligand, and it was used for the synthesis of a new series of binuclear Ph_2PPy-bridged complexes. Treatment of 1 with $[Rh(CO)_2Cl]_2$ in dichloromethane yielded $[(\eta^5\text{-}C_5H_5)Rh(\mu\text{-}CO)(\mu\text{-}Ph_2PPy)Rh(CO)Cl]$ (2) as a red-brown, microcrystalline solid that was stable for long periods both in the solid and in solution. It is a nonelectrolyte in benzene. The molecular structure of 2 is shown in Figure 1. In accordance with X-ray structure, the IR spectrum indicated the presence of both terminal and bridged carbonyl ligands; the stretching frequency of the terminal CO is consistent with it being bound trans to the nitrogen atom. The ^1H NMR signal of the cyclopentadienyl group consists of a double doublet at δ 5.30 (J = 0.8, 1.1 Hz) due to coupling to ^{103}Rh and ^{31}P.[9-14,16]

The ^{13}C NMR spectrum of 2 shows a ^{13}CO resonance at δ 224.5 due to the bridging carbonyl and a resonance at δ 188.2 due to the terminal carbonyl. Interchange of these carbonyls was not detected. The bridging carbonyl shows three couplings of 13, 33, and 58 Hz to the two ^{103}Rh and the ^{31}P nuclei, but the assignments are unknown. The terminal carbonyl shows $^1J(^{103}Rh-^{13}C) = 68$ Hz and $^2J(^{103}Rh-^{13}C) = {}^3J(^{31}P-^{13}C)$ = ca. 2.5 Hz. J modulation[17] was used to distinguish between C and CH carbon signals in the aromatic region of the spectrum. This, coupled with the chemical shifts, permitted the unambiguous assignment of C(2), C(4), and C(6) of the pyridine and two C(1) of the phenyl rings. The remaining assignments are ten-

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Table I. Crystal and Refinement Data

formula	$C_{24}H_{19}ClNO_2PRh_2$	$C_{23}H_{19}I_3NOPRh_2$
fw	625.7	942.9
cryst system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a, Å	15.928 (2)	7.847 (1)
b, Å	11.322 (2)	16.995 (2)
c, Å	26.646 (4)	19.446 (3)
β, deg	104.2 (2)	96.4 (1)
V, Å^3	4657.6	2577.3
Z	8	4
d_{calcd}, g/cm^3	1.79	2.60
cryst size, mm	0.10 × 0.15 × 0.13	0.12 × 0.15 × 0.15
orientatn reflectn, no., range (2θ)	20, $15 < 2\theta < 28$	20, $15 < 2\theta < 28$
T, °C	22	21
abs coeff, cm^{-1}	14.7	47.2
radiatn, Å	Mo Kα, $\lambda = 0.71069$	Mo Kα, $\lambda = 0.71069$
monochromator	graphite crystal	graphite crystal
scan type	$\omega-\theta$	$\omega-\theta$
scan speed, s^{-1}	0.03	0.03
scan range, deg	1.2	1.2
reflctns measd	$\pm h,+k,+l$	$\pm h,+k,+l$
std reflctns		3 measd after every 110′
data limits	$3 < 2\theta < 52$	$3 < 2\theta < 50$
obsd data	4383 [$I \geq 3\sigma(I)$]	3152 [$I \geq 3\sigma(I)$]
no. of parameters refined	510	281
R	0.042	0.026
R_w	0.047	0.030
largest shift esd in final cycle	0.20	0.25
largest peak, e/Å^3	0.75	0.45

Table II. Selected Bond Lengths (Å) and Angles (deg) for $[(\eta^5-C_5H_5)Rh(\mu-CO)(\mu-Ph_2PPy)Rh(CO)Cl]$

	Bond Lengths		
Rh(1)–Rh(2)	2.648 (1)	Rh(1A)–Rh(2A)	2.658 (1)
Rh(1)–P(1)	2.222 (2)	Rh(1A)–P(1A)	2.225 (3)
Rh(1)–C(0)	1.890 (9)	Rh(1A)–C(0A)	1.935 (10)
Rh(1)–C(1)	2.215 (12)	Rh(1A)–C(1A)	2.289 (11)
Rh(1)–C(2)	2.225 (13)	Rh(1A)–C(2A)	2.269 (11)
Rh(1)–C(3)	2.263 (11)	Rh(1A)–C(3A)	2.240 (10)
Rh(1)–C(4)	2.288 (12)	Rh(1A)–C(4A)	2.216 (10)
Rh(1)–C(5)	2.299 (14)	Rh(1A)–C(5A)	2.261 (11)
Rh(1)–Cp*	1.925 (12)	Rh(1A)–Cp*(A)	1.909 (10)
Rh(2)–Cl(1)	2.346 (3)	Rh(2A)–Cl(1A)	2.360 (3)
Rh(2)–N(1)	2.107 (8)	Rh(2A)–N(1A)	2.132 (8)
Rh(2)–C(0)	2.048 (10)	Rh(2A)–C(0A)	2.085 (8)
Rh(2)–C(6)	1.814 (14)	Rh(2A)–C(6A)	1.801 (12)
P(1)–C(7)	1.877 (9)	P(1A)–C(7A)	1.824 (9)
P(1)–C(12)	1.787 (9)	P(1A)–C(12A)	1.814 (9)
P(1)–C(18)	1.845 (9)	P(1A)–C(18A)	1.852 (9)
N(1)–C(7)	1.338 (11)	N(1A)–C(7A)	1.343 (11)
N(1)–C(11)	1.366 (13)	N(1A)–C(11A)	1.307 (13)
O(1)–C(6)	1.120 (18)	O(1A)–C(6A)	1.178 (14)
O(2)–C(0)	1.198 (13)	O(2A)–C(0A)	1.151 (12)
	Bond Angles		
Rh(1)–C(0)–Rh(2)	84.4 (4)	Rh(1A)–C(0A)–Rh(2A)	82.7 (4)
Rh(1)–Rh(2)–C(0)	45.3 (2)	Rh(1A)–Rh(2A)–C(0A)	46.2 (2)
Rh(1)–Rh(2)–C(6)	83.0 (5)	Rh(1A)–Rh(2A)–C(6A)	82.0 (3)
Rh(1)–Rh(2)–N(1)	94.3 (2)	Rh(1A)–Rh(2A)–N(1A)	95.9 (2)
Rh(1)–Rh(2)–Cl(1)	167.1 (1)	Rh(1A)–Rh(2A)–Cl(1A)	165.3 (1)
Rh(1)–P(1)–C(18)	112.3 (3)	Rh(1A)–P(1A)–C(18A)	113.9 (4)
Rh(1)–P(1)–C(12)	116.3 (3)	Rh(1A)–P(1A)–C(12A)	116.6 (3)
Rh(1)–P(1)–C(7)	115.2 (3)	Rh(1A)–P(1A)–C(7A)	114.3 (3)
Rh(2)–Rh(1)–C(0)	50.3 (3)	Rh(2A)–Rh(1A)–C(0A)	51.1 (3)
Rh(2)–Rh(1)–P(1)	82.1 (1)	Rh(2A)–Rh(1A)–P(1A)	79.9 (1)
Rh(2)–N(1)–C(11)	119.8 (7)	Rh(2A)–N(1A)–C(11A)	124.2 (7)
Rh(2)–N(1)–C(7)	122.9 (7)	Rh(2A)–N(1A)–C(7A)	117.2 (6)
Rh(2)–Rh(1)–Cp*	137.5 (4)	Rh(2A)–Rh(1A)–Cp*(A)	141.7 (4)
C(O)–Rh(2)–C(6)	98.7 (5)	C(0A)–Rh(2A)–C(6A)	100.1 (4)
N(1)–Rh(2)–C(6)	174.8 (5)	N(1A)–Rh(2A)–C(6A)	176.4 (4)
N(1)–Rh(2)–C(0)	82.3 (3)	N(1A)–Rh(2A)–C(0A)	80.4 (4)
Cl(1)–Rh(2)–C(6)	90.3 (4)	Cl(1A)–Rh(2A)–C(6A)	90.4 (4)
Cl(1)–Rh(2)–C(0)	147.3 (3)	Cl(1A)–Rh(2A)–C(0A)	148.2 (3)
Cl(1)–Rh(2)–N(1)	91.5 (2)	Cl(1A)–Rh(2A)–N(1A)	90.9 (2)
C(0)–Rh(1)–Cp*	134.3 (4)	C(0A)–Rh(1A)–Cp*(A)	134.5 (4)
Rh(2)–C(6)–O(1)	172.0 (1)	Rh(2A)–C(6A)–O(1A)	173.9 (9)
N(1)–C(7)–P(1)	112.8 (6)	N(1A)–C(7A)–P(1A)	117.7 (7)
C(11)–N(1)–Rh(2)	119.8 (6)	C(11A)–N(1A)–Rh(2A)	124.2 (7)
C(11)–N(1)–C(7)	117.2 (8)	C(11A)–N(1A)–Rh(2A)	118.7 (8)
P(1)–Rh(1)–Cp*	129.1 (4)	P(1A)–Rh(1A)–Cp*(A)	130.0 (4)

tative, being based on chemical shift, $J(^{31}P-^{13}C)$, and intensity.[18] The cyclopentadienyl signal at δ 90.2 is a double doublet due to coupling to ^{103}Rh and ^{31}P. Both the ^1H and ^{13}C NMR spectra show that the two phenyl groups of the Ph_2PPy ligands are inequivalent, as required by the X-ray structure.

The ^{103}Rh NMR spectrum of **2** shows two signals at δ 472 and –1119 ($^1J(^{103}Rh-^{31}P)$ = 178 Hz). The signals can be assigned on the basis of $J(^{103}Rh-^{31}P)$ as δ 472 to Rh(2) and δ –1119 to Rh(1). The chemical shift of Rh(2) is in the normal region for rhodium(I) complexes.[19] The chemical shift of Rh(1) is outside the range normally found for rhodium(I) complexes, which are rarely at a frequency lower than δ –800. The closely related $[Rh(\eta^5-C_5H_5)(C_2H_4)_2]$ is at δ –762. To date the low-frequency ^{103}Rh shifts of noncluster complexes are associated with the $(C_5R_5)Rh$ groups (R = H, Me).[20] The value of $^1J(^{103}Rh-^{31}P)$ of 178 Hz, compared with 199.8 Hz in **1**, and $\delta(^{31}P)$ 52.1, compared with 53.8 in **1**, are consistent with Rh(1) remaining effectively rhodium(I) in **2**. The $^{31}P\{^1H\}$ NMR spectrum of **2**, in $CDCl_3$ solution, showed a double doublet at δ 52.1 [$^1J(^{103}Rh-^{31}P)$ = 175.6 Hz; $^2J(^{103}Rh-^{31}P)$ = 5.3 Hz] in accordance with the presence of a rhodium–rhodium bond in the molecule.

The attempts to synthesize the heterobinuclear Ph_2PPy-bridged rhodium–rhodium complex analogous to **2** by reacting $[Ir(CO)_2(p\text{-toluidine})Cl]$ with **1** in benzene afforded the complex $[(\eta^5-C_5H_5)Rh(\mu-CO)(\mu-Ph_2PPy)Ir(CO)Cl]$ (**3**) as a yellow solid in moderate yield. Unfortunately, we are not able to obtain it in analytically pure form, and its formulation is based on the spectroscopic data which indicate a structure for **3** that is analogous to that for **2** [ν(CO) 2000 and 1780 cm^{-1}; $\delta(C_5H_5)$ 5.16, $^2J(^{103}Rh-^1H)$ = 0.7 Hz, $^3J(^{31}P-^1H)$ = 1.2 Hz]. Compounds with a direct rhodium–iridium bond are very few; principally they are mixed-metal clusters.[21-24] Compound **3**

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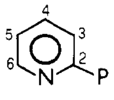
[18] Numbering convention for Ph_2PPy:



There is rotation of the phenyl groups making the ortho and meta hydrogen and carbon atoms pairwise equivalent. δ(C(2)) 160.0, $^1J(^{13}C-^{31}P)$ = 68 Hz; δ(C(3)) 127.4, $^2J(^{13}C-^{31}P)$ = 11 Hz; δ(C(4)) 138.2, $^3J(^{13}C-^{31}P)$ = 4 Hz; δ(C(5)) 125.7; δ(C(6)) 153.5, ^3J = 13 Hz; $P-C(Ph)_{quaternary}$ δ 136.2, $^1J(^{13}C-^{31}P)$ 45 Hz; δ 133.7, $^1J(^{13}C-^{31}P)$ = 44 Hz; δ(*o*-Ph) = 133.7, $J(^{13}C-^{31}P)$ = 13 Hz; δ(*o*-Ph) = 132.9, $J(^{13}C-^{31}P)$ = 12 Hz; δ(*m*-Ph) = 128.9, $J(^{13}C-^{31}P)$ = 11 Hz; δ(*m*-Ph) 127.4, $J(^{13}C-^{31}P)$ = 11 Hz; δ(*p*-Ph) 131.3, $J(^{13}C-^{31}P)$ = 0 Hz; δ(*p*-Ph) 131.2, $J(^{13}C-^{31}P)$ = 0 Hz; $\delta(C_5H_5)$ 90.2, $J(^{13}C-^{31}P)$ = 2.7 and 3.8 Hz.

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is unstable both as the solid and in solution; this prevented an extensive study of its reactivity.

Molecular Structure of [(η^5-C_5H_5)Rh(μ-CO)(μ-Ph_2PPy)Rh(CO)Cl] (2). The unit cell contains two crystallographically independent molecules that have very similar structures. A perspective view and the numbering scheme of one molecule is presented in Figure 1. Selected bond distances and angles are presented in Table II. The only distances that differ by more than 3σ between the two molecules are Rh(1)–Rh(2) (0.010 Å), Rh(2)–C(1) (0.014 Å), Rh(2)–N(1) (0.025 Å), Rh(1)–C(CO) (0.045 Å), and Rh(2)–C(CO) (0.036 Å). These differences are probably a consequence of packing effects, and little chemical significance can be placed on them. In all tables the second molecule is labeled as A.

The structure is characterized by the short Rh(1)–Rh(2) bond distance, by the different coordination geometry of the two rhodium atoms, and by the presence of asymmetric CO bridging ligand. The rhodium–rhodium distance of 2.648 (1) Å falls in the range normally associated with the Rh–Rh single bond and is significantly shorter than the intraligand P···N separation of 2.695 Å, indicating a compression along the Rh(1)–Rh(2) axis as expected for a metal–metal bonded system. The coordination geometry about the rhodium centers is very different. The ligands about Rh(1) are disposed in an approximately tetrahedral coordination geometry if the η^5-cyclopentadienyl ligand is regarded as occupying a single coordination site by the centroid of the cyclopentadienyl ring (Cp*); the phosphorus atom of the Ph_2PPy, the carbon of the bridging carbon monoxide, and the Rh(2) atoms complete the coordination sphere of Rh(1). Rh(2) is formally five-coordinate: the nitrogen atom of the bridging Ph_2PPy, the Rh(1), the chlorine, and the carbon atoms of the terminal and bridging carbon monoxide occupying the coordination sites. The Cl(1), C(6), Rh(1), and N(1) atoms are in a pseudo square-planar arrangement, and the Rh(2) coordination geometry is that of a distorted square pyramid with the vertex shifted toward the Rh(1)–Rh(2) vector; this is shown by the Cl(1)–Rh(2)–C(0) bond angle of 147.3 (3)°. In the Cl(1)C(6)Rh(1)N(1) pseudo square-planar plane, major deviations are observed with the Cl(1) atom; in fact while N(1)–Rh(2)–C(6) bond angle is nearly linear [174.8 (4)°], the Cl(1)–Rh(2)–Rh(1) bond angle is 167.1 (1)°. This may be also to minimize nonbonded contacts between Cl(1) and the pyridine ring [Cl(1)···C(11) = 3.23 (1) Å]; in agreement the Cl(1)Rh(2)N(1)C(11) and N(1)Rh(2)Rh(1)P(1) torsion angles are −34.7 (2)° and 26.9 (1)°, respectively. The Ph_2PPy is twisted about the Rh(1)–Rh(2) bond such that nitrogen on the Rh(2) and phosphorus on the Rh(1) metals reduce the unfavorable contacts of the pyridine ring with Cl(1) and of the phenyl groups with the cyclopentadienyl ring. The structural features of the cyclopentadienyl ligand are essentially the same as in the bimetallic cyclopentadienyl rhodium(I) complexes.[9–14,25] The cyclopentadienyl ring is located on the less hindered side of the molecule, and the angles at Rh(1) between the centroid of the cyclopentadienyl ring Cp* and the other ligands are larger than those expected for a tetrahedral coordination [Rh(2)–Rh(1)–Cp* = 137.5 (2)°, P(1)–Rh(1)–Cp* = 129.1 (3)°, C(0)–Rh(1)–Cp* 134.3 (3)°; in the other crystallographically independent molecule these values are respectively 141.7 (2)°, 129.9 (3)°, and 134.5 (3)°]. The separation Rh(1)–Cp* is 1.925 (12) Å [1.909 (12) Å in the other molecule] while the Rh(1)–C(Cp*) ranges in both the molecules from 2.215 (12) to 2.299 (12) Å. These values are in agreement with literature reports.[9–14,25,26] The Rh(2)–N(1) [2.107 (7) Å], Rh(1)–P(1) [2.222 (2) Å], and Rh(2)–Cl(1) [2.346 (3) Å] bond distances are comparable with the corresponding averaged values of 2.115 (5), 2.210 (1), and 2.355 (1) Å in the A-frame complex [$Rh_2(Ph_2PPy)_2$(μ-CO)Cl_2].[6a] The bridging carbonyl is asymmetric in the Colton and McCormick classification[27] with Rh(1)–C(0) and Rh(2)–C(0) bond distances of 1.890 (1) and 2.048 (1) Å. The asymmetric bonding is not accompanied by a significant variation in the internal Rh(1)–C(CO)–Rh(2) angle [84.4 (4)°] with respect to the values given for symmetrical bridges (83°). On the other hand, the difference in the Rh(1)–C(CO)–O(2) and Rh(2)–C(CO)–O(2) bond angles of 25° [150.3 (8)° and 125.3 (7)°, respectively] indicates that the carbonyl should be considered more as semibridging rather than asymmetric bridging.

Reaction of [(η^5-C_5H_5)Rh(μ-CO)(μ-Ph_2PPy)Rh(CO)Cl] (2) with Small Molecules. Treating a diethyl ether solution of **2** briefly with gaseous sulfur dioxide led to a yellow-orange solution from which were deposited orange crystals of [(η^5-C_5H_5)Rh(μ-Ph_2PPy)(μ-SO_2)Rh(CO)Cl] (**4**). The IR spectrum of **4** in the carbonyl region showed only one terminal ν(CO) band at higher frequency than in the precursor; the ^1H and $^{31}P\{^1H\}$ NMR showed the same pattern observed for the precursor **2**, indicating that the metal–metal bond is retained in the process. These data suggest that the bridging carbonyl ligand has been replaced by sulfur dioxide. The presence of the bridging sulfur dioxide is also supported by the values of ν(SO) at 1060 and 1200 cm^{-1} which compare well with those reported for SO_2 ligands bridging a metal-metal bond.[28]

Slow addition of Cl_2 or Br_2 to a dichloromethane solution of **2** afforded yellow-orange compounds which, on the basis of analytical, IR spectroscopic, and conductivity data, must be formulated as [(η^5-C_5H_5)X_2Rh(μ-Ph_2PPy)Rh(CO)X_3] (**5**, X = Cl; **6**, X = Br). Conductivity measurements, performed on dichloromethane solutions, are in accord with their formulation as neutral species; their IR spectra show only one ν(CO) at values shifted by ca. 80–100 cm^{-1} to higher frequency than in the precursor, i.e. at values consistent with terminal CO in rhodium(III) complexes. The low solubility of **5** and **6** prevented reliable NMR spectra.

The most interesting reaction with halogens was observed when the oxidative addition to **2** was performed with iodine; in this case the reaction yielded a solid mixture of [(η^5-C_5H_5)Rh(μ-I)(μ-Ph_2PPy)Rh(CO)I_2] (**7**) and [(η^5-C_5H_5)I_2Rh(μ-Ph_2PPy)Rh(CO)I_3] (**8**) which could be separated by their different solubilities in benzene. Compound **7** can be considered the product of the first step of the oxidative process; in fact the addition of I_2 to **7** gives the rhodium(III) compound **8**, analogous to **5** and **6**. Compound **7** has been fully characterized by X-ray analysis, and its structure is shown in Figure 2. The presence of one bridging halogen atom in **5**, **6**, and **8**, to make both the rhodium atoms coordinatively saturated 18-electron species, is probable in the light of the crystal structure of **7**. Compounds such as **7** could not be detected in the reactions with Cl_2 and Br_2. This could be a consequence

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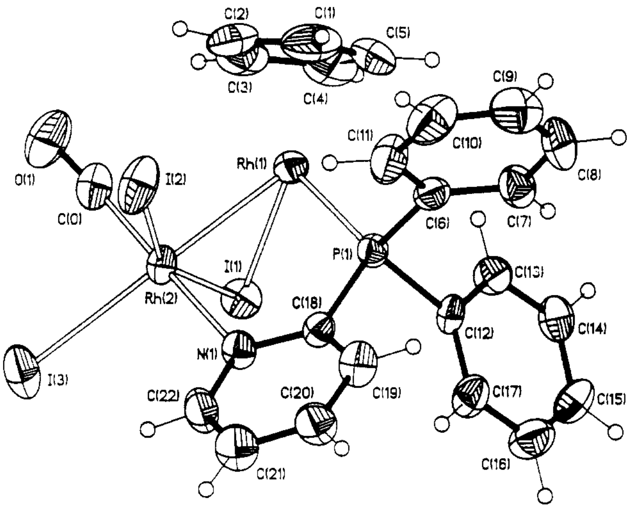

Figure 2. View of the molecule $[(\eta^5\text{-}C_5H_5)Rh(\mu\text{-}I)(\mu\text{-}Ph_2PPy)\text{-}Rh(CO)I_2]$.

either of a lower activation energy for the second step of the process (possibly due to the bulk of iodine reducing the rate of the second step) or of a different mechanism which could be operating in the latter case. The latter hypothesis was supported by formation of 7 as major reaction product of 2 with CH_2Cl_2. On the other hand, it is also well-known that the attack of iodine on some bimetallic iridium(I) complexes proceeds through a radical mechanism.[29]

Complex 7 can be either formulated as a Rh^I–Rh^{III} or as a Rh^{II}–Rh^{II} derivative. The rhodium–rhodium bond would be the result of electron pair donation from the 18-electron rhodium atom to 16-electron rhodium atom (bearing the iodine atoms) in the former case or a d^7–d^7 bonding interaction between the two Rh^{II} centers in the latter. Spectroscopic IR and ^1H NMR data were consistent with 7 being a Rh^{II}–Rh^{II} species. The ^1H NMR spectra of 7 and 8 showed the same pattern for the cyclopentadienyl proton resonance but different coupling constants with the phosphorus and rhodium atoms [$\delta(C_5H_5)$ 5.54, $^2J(^{103}Rh–^1H) = 0.60$ Hz, $^3J(^{31}P–^1H) = 2.19$ Hz for 8; $\delta(C_5H_5)$ 5.47, $^2J(^{103}Rh–^1H) = 0.60$ Hz, $^3J(^{31}P–^1H) = 1.66$ Hz for 7]. Of particular interest is the magnitude of $^3J(^{31}P–^1H)$; in fact for the same kind of complexes these coupling constants have been related to the oxidation state of the rhodium atom in cyclopentadienyl(phosphine)rhodium complexes.[17,30] Note that $^3J(^{31}P–^1H)$ for 7 is intermediate between that of the starting material 2 in which the rhodium atoms are in a formal oxidation number of +1 and that of the oxidative addition product 8. Compounds 7 and 8 were the only products obtained from the reaction of 2 with CH_2I_2; no evidence for the formation of μ-CH_2 species has been obtained. We have been unable to separate the mixture of products obtained in the reaction of 2 with CH_3I.

Molecular Structure of $[(\eta^5\text{-}C_5H_5)Rh(\mu\text{-}I)(\mu\text{-}Ph_2PPy)Rh(CO)I_2]$ (7). The experimental details, including the crystal parameters, are reported in Table I. A perspective view of the molecule with the atomic labeling scheme is shown in Figure 2. Selected bond distances and angles are given in Table III.

Table III. Selected Bond Lengths (Å) and Angles (deg) for $[(\eta^5\text{-}C_5H_5)Rh(\mu\text{-}I)(\mu\text{-}Ph_2PPy)Rh(CO)I_2]$

Bond Lengths			
Rh(1)–Rh(2)	2.686 (1)	C(0)–O(1)	1.150 (9)
Rh(1)–I(1)	2.630 (1)	Rh(2)–I(1)	2.648 (1)
Rh(1)–C(1)	2.155 (8)	Rh(2)–C(0)	1.811 (8)
Rh(1)–C(2)	2.219 (8)	Rh(2)–I(2)	2.647 (1)
Rh(1)–C(3)	2.229 (8)	Rh(2)–I(3)	2.812 (1)
Rh(1)–C(4)	2.210 (8)	Rh(2)–N(1)	2.153 (5)
Rh(1)–C(5)	2.184 (8)	P(1)–C(6)	1.819 (7)
Rh(1)–Cp*	1.847 (8)	P(1)–C(12)	1.829 (7)
N(1)–C(18)	1.346 (9)	P(1)–C(18)	1.832 (6)
N(1)–C(22)	1.331 (9)		

Bond Angles			
Rh(1)–Rh(2)–I(1)	59.1 (1)	Rh(2)–Rh(1)–I(1)	59.7 (1)
Rh(1)–Rh(2)–I(2)	96.2 (1)	Rh(2)–Rh(1)–P(1)	86.3 (1)
Rh(1)–Rh(2)–I(3)	156.5 (1)	Rh(2)–Rh(1)–Cp*	131.3 (1)
Rh(1)–Rh(2)–C(0)	86.5 (3)	Rh(2)–C(0)–O(1)	176.9 (7)
Rh(1)–Rh(2)–N(1)	94.7 (1)	Rh(2)–N(1)–C(18)	121.9 (4)
Rh(1)–P(1)–C(18)	116.4 (2)	Rh(2)–N(1)–C(22)	118.4 (5)
Rh(1)–P(1)–C(12)	116.0 (2)	C(18)–N(1)–C(22)	116.8 (6)
Rh(1)–P(1)–C(6)	114.8 (2)	N(1)–C(18)–C(19)	122.7 (6)
P(1)–C(18)–N(1)	116.9 (5)	N(1)–Rh(2)–I(2)	84.5 (2)
P(1)–C(18)–C(19)	120.3 (5)	N(1)–Rh(2)–C(0)	172.8 (3)
P(1)–C(6)–C(11)	118.2 (6)	N(1)–Rh(2)–I(3)	97.8 (1)
P(1)–C(6)–C(7)	122.6 (6)	Rh(1)–I(1)–Rh(2)	61.2 (1)
P(1)–Rh(1)–Rh(2)	86.3 (1)	I(1)–Rh(2)–I(2)	155.1 (1)
P(1)–Rh(1)–I(1)	91.9 (1)	I(1)–Rh(2)–I(3)	100.3 (1)
P(1)–Rh(1)–Cp*	129.7 (7)	I(1)–Rh(2)–C(0)	93.2 (2)
P(1)–C(12)–C(13)	117.2 (5)	I(3)–Rh(2)–I(2)	104.6 (1)
P(1)–C(12)–C(17)	124.2 (5)	I(3)–Rh(2)–C(0)	83.5 (3)
		I(2)–Rh(2)–C(0)	88.3 (3)

The rhodium atoms are bridged by the Ph_2PPy and I(1) ligands. The Rh(1) atom has a distorted tetrahedral coordination geometry, the coordination positions being occupied by the centroid of the cyclopentadienyl ring (Cp*), the phosphorus atom of the Ph_2PPy ligand, and the iodine of μ-I(1). The bond angles at Rh(1) atom deviate from tetrahedral coordination, as is observed in 2 and in other bimetallic cyclopentadienylrhodium complexes[9–14] as a consequence of the η^5-bonding mode of the cyclopentadienyl ring to the metal.

The Rh(2) atom displays a distorted octahedral coordination with Rh(2)I(2)C(CO)I(1)N(1) atoms in the equatorial plane and the I(3) and Rh(1) atoms in the apical sites. Significant deviations from octahedral geometry are observed with I(3) and I(1). The I(3) atom lies −1.136 Å out the Rh(2)Rh(1)N(1)C(CO) plane, presumably in order to minimize contacts with I(1), I(2), and the carbonyl carbon atom. In fact the I(1)···I(3) separation of 4.192 Å and I(2)···I(3) separation of 4.321 Å are shorter than the sum of the van der Waals radii; the I(3)···C(CO) and I(2)···C(CO) separations are 3.167 and 3.163 Å, respectively. The terminal Rh–I distances are very different, the Rh(2)–I(2) and Rh(2)–I(3) distances being 2.647 (1) and 2.812 (1) Å, respectively. We do not understand the cause of this unusual lengthening of the Rh(2)–I(3) bond, but it is probably a consequence of the almost trans position of I(3) to the Rh(1)–Rh(2) bond. The present value of 2.812 (1) Å is significantly longer than the values of 2.757 (2) and 2.761 (2) Å reported for the bimetallic complexes $[Rh_2(\mu\text{-}dmpz)(\mu\text{-}dppm)(CO)_2I_2]^+$ [31] (dmpz = 3,5-dimethylpyrazolate) and $[Rh_3(C_6H_5CH_2NC)_{12}I_2]^{3+}$,[32] respectively, in which the terminal Rh–I is trans to the Rh–Rh bond,

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and compares well with the values of 2.865 and 2.851 Å found for the bridging Rh–I distance in $[Rh_3(\mu\text{-dpmp})_2(CO)_3I_2]^+$ [33,34] (dpmp = bis(diphenylphosphino)methyl)-phenylphosphine) complex. Surprisingly, the terminal Rh(2)–I(2) bond distance of 2.647 (1) Å compares well with the two bridging Rh(2)–I(1) and Rh(1)–I(1) values of 2.648 (1) and 2.630 (1) Å, respectively. The latter are among the shortest bridging Rh–I bond distances so far reported and compare well with the corresponding values found for $[Rh_3(\mu\text{-dpmp})_2(CO)I_4]^+$.[33,34] The geometry of the bridging iodo ligand appears normal although there is some asymmetry. The Rh(1)–I(1) bond distance is shorter than the Rh(2)–I(1) distance by 0.018 Å. This asymmetry is not unexpected when the unsymmetrical nature of the entire molecule is considered.

The Rh(1)–Rh(2) distance of 2.686 (1) Å is only 0.038 Å longer than it is in **2** and indicates that the metal–metal bond was retained.

The structural features of the bridging Ph_2PPy rigid ligand are essentially the same as in **2**, the Rh(2)–Rh(1)–P(1), Rh(1)–Rh(2)–N(1), and P(1)–C(18)–N(1) bond angles being 86.3 (1)°, 94.7 (1)°, and 116.9 (5)°, respectively. The Ph_2PPy is twisted about the Rh–Rh bond so that the nonbonded contact between the cyclopentadienyl ligand and a phenyl group is minimized [C(5)···C(6) = 3.615 Å], as reflected in the Rh(1)–Rh(2)–N(1) and P(1)–Rh(1)–Rh(2) bond angles of 94.7 (1) and 86.3 (1)°, respectively.

The cyclopentadienyl ring is located on the less hindered side of the molecule. The Rh(1)–C(C_5H_5) distances and the Rh(1)–Cp* separation are very similar to those found in **2** and analogous rhodium–cyclopentadienyl systems.

Concluding Remarks

The presence of two rhodium(I) centers in **2** offers the possibility to activate small molecules such as SO_2, halogens, alkyl halides, olefins, and acetylenes by oxidative addition. The results show that SO_2 adopts a bridging bonding mode in the product of its reaction with **2**, although initial attack of the electrophile on a terminal position cannot be excluded. This seems to happen regardless of the theoretical ability of each metal center to react independently. In fact, the ability of 16-electron rhodium(I) center and 18-electron five-coordinate cyclopentadienylrhodium(I) complexes to add molecules such as SO_2 was determined. Oxidative addition to one of the metals was not observed in the reactions of **2** with halogens and CH_3I. These results are rather surprising if we consider that the metal centers in **2** are very different in basicity and coordination number. Bosnich[35] studied oxidative addition and reductive elimination reactions on homobimetallic complexes of rhodium(I) and iridium(I) containing bis(phosphino)pyrazole as the binucleating ligand and observed that oxidative addition at one center leads to deactivation at the other. This appears to be principally an electronic effect in that the lower oxidation state metal transfers some of its electron charge to the higher oxidation state metal via the bridging ligand. We suspect that an analogous process operates in unsymmetrical bimetallic complexes in which the metal centers are held in close proximity by a metal–metal bond and a rigid bridging ligand, as in **2**. Here the electron density on the two metals is balanced before oxidative addition via the metal–metal bond; this effect may help explain the unique reactivity pattern observed.

Experimental Section

Compounds $[Rh(CO)_2Cl]_2$,[36] $[Rh(\eta^5\text{-}C_5H_5)(CO)_2]$,[37] $[Rh(\eta^5\text{-}C_5H_5)_2(CO)_3]$,[38] and $[Ir(CO)_2Cl(p\text{-toluidine})]$[39] were prepared by literature methods. All other reagents were purchased and used as supplied. Solvents were dried by standard procedures. All experiments were performed under an atmosphere of purified nitrogen. IR spectra were obtained on Nujol mulls by using a Perkin-Elmer 783 spectrophotometer. ^1H and ^{31}P NMR spectra were recorded on a Bruker WP8O-SY spectrometer, operating at 80.13 and 32.442 MHz, respectively. ^{13}C and ^{103}Rh NMR spectra were recorded on a Bruker WH 400 spectrometer, operating at 100.66 and 12.66 MHz, respectively. ^1H and ^{13}C NMR spectra were referenced to internal tetramethylsilane, ^{31}P spectra to external 85% H_3PO_4, and ^{103}Rh spectra to ^{103}Rh, 3.16 MHz. In all cases the currently approved sign convection, in which high frequency is positive, was used (IUPAC, 1976). Conductivity measurements were made with a Radiometer CDM 3 conductivity meter.

Preparation of $[Rh(\eta^5\text{-}C_5H_5)(CO)(Ph_2PPy)]$ (1). $[Rh(\eta^5\text{-}C_5H_5)(CO)_2]$ [obtained in heptane from $[Rh(CO)_2Cl]_2$ (0.250 g, 0.643 mmol) and an excess of $Tl(C_5H_5)$] and a slight excess of Ph_2PPy were refluxed in heptane (200 mL) for about 5 h. During this time a color change from yellow to orange occurred. The completion of the reaction was checked by the disappearance of the ν(CO) absorptions related to $[Rh(\eta^5\text{-}C_5H_5)(CO)_2]$. The solution was then concentrated to ca. 50 mL and chromatographed on a neutral alumina column (2 × 20 cm) saturated with hexane. Elution with diethyl ether of the orange band, followed by slow evaporation of the solvent, gave the product as orange crystals, yield 0.531 g (1.157 mmol), 90%. The product was analogously obtained starting from $[Rh(\eta^5\text{-}C_5H_5)_2(CO)_3]$. Anal. Calcd for $C_{23}H_{19}NOPRh$: C, 60.15; H, 4.17; N, 3.05. Found: C, 60.26; H, 4.20; N, 3.06. IR (KBr, Nujol): ν(CO) 1940 cm^{-1}. ^1H NMR (CD_2Cl_2): δ 5.18 (t, $^2J_{RhH} = {}^3J_{PH} = 0.6$ Hz, C_5H_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 53.80 (d, $^1J_{RhP} = 199.8$ Hz).

Preparation of $[(\eta^5\text{-}C_5H_5)Rh(\mu\text{-}CO)(\mu\text{-}Ph_2PPy)Rh(CO)Cl]$ (2). $[Rh(CO)_2Cl]_2$ (0.0845 g, 0.2175 mmol) and $[Rh(\eta^5\text{-}C_5H_5)(CO)(Ph_2PPy)]$ (**1**) (0.200 g, 0.345 mmol) were dissolved in dichloromethane (40 mL), and the resulting solution was stirred for ca. 1 h. By addition of diethyl ether–hexane (1:2) (60 mL) to the reaction mixture the product was formed as a red-brown microcrystalline solid (0.245 g, 0.3915 mmol) in 90% yield. Anal. Calcd for $C_{24}H_{19}ClNO_2PRh_2$: C, 46.07; H, 3.06; N, 2.24; Cl, 5.66. Found: C, 46.15; H, 3.10; N, 2.24; Cl, 5.62. IR (KBr, Nujol): ν(CO) 2000, 1820 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.30 (dd, $^2J_{RhH} = 0.8$, $^3J_{PH} = 1.1$ Hz, C_5H_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 52.10 (dd, $^1J_{RhP} = 175.6$, $^2J_{RhP} = 5.3$ Hz).

Preparation of $[(\eta^5\text{-}C_5H_5)Rh(\mu\text{-}CO)(\mu\text{-}Ph_2PPy)Ir(CO)Cl]$ (3). A benzene solution (20 mL) of **1** (0.134 g, 0.291 mmol) was added dropwise to a stirred solution of $[Ir(CO)_2(p\text{-toluidine})Cl]$ (0.119 g, 0.307 mmol) in the same solvent (60 mL). A slight excess of $[Ir(CO)_2(p\text{-toluidine})Cl]$ is necessary to reduce the formation of byproducts. The reaction mixture was stirred for 4 h and then *n*-hexane added to induce the precipitation of the product (together with a little amount of a byproduct as shown by IR spectra) as a pale yellow powder. The solution, containing also starting $[Ir(CO)_2(p\text{-toluidine})Cl]$, was syringed off and the yellow precipitate washed with *n*-hexane and dried in vacuo; yield 0.145 g (0.187 mmol), 70%. All attempts to obtain the product in pure form failed owing to its instability in solution. IR (KBr, Nujol): ν(CO) 2000, 1780 cm^{-1}. ^1H NMR (C_6D_6): δ 5.16 (dd, $^2J_{RhH} = 0.7$, $^3J_{PH} = 1.2$ Hz, C_5H_5).

Preparation of $[(\eta^5\text{-}C_5H_5)Rh(\mu\text{-}Ph_2PPy)(\mu\text{-}SO_2)Rh(CO)Cl]$ (4). When sulfur dioxide was bubbled through a diethyl ether solution (60 mL) of **2** (0.060 g, 0.0096 mmol), an orange powder

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soon precipitated. The solvent was then removed by syringe and the crude product recrystallized from dichloromethane–hexane (1:3) to give compound **4** as an orange, microcrystalline solid (0.059 g, 0.090 mmol) in 94% yield. Anal. Calcd for $C_{23}H_{19}ClNO_3PRh_2S$: C, 41.75; H, 2.89; N, 2.11; Cl, 5.35; S, 4.84. Found: C, 41.78; H, 2.98; N, 2.12; Cl, 5.41; S, 4.84. IR (KBr, Nujol): ν(CO) 2030, ν(SO) 1060, 1200 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.37 (dd, $^2J_{RhH} = 0.75$, $^3J_{PH} = 1.46$ Hz, C_5H_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 60.3 (dd, $^1J_{RhP} = 162.2$, $^2J_{RhP} = 3.8$ Hz).

Reaction of 2 with Chlorine. Complex **2** (0.100 g, 0.159 mmol) was dissolved in dichloromethane (50 mL), and chlorine was bubbled through the solution. Immediately the color of the solution turned from red-brown to orange. The volume of the solution was then reduced to ca. 15 mL. By addition of hexane (30 mL) a yellow-orange precipitate was obtained. This was filtered, washed with diethyl ether, and dried in vacuo to give $[(\eta^5\text{-}C_5H_5)Cl_2Rh(\mu\text{-}Ph_2PPy)Rh(CO)Cl_3]$ (**5**) (0.087 g, 0.117 mmol) in 74% yield. Anal. Calcd for $C_{23}H_{19}Cl_5NOPRh_2$: C, 37.35; H, 2.6; N, 1.89; Cl, 23.97. Found: C, 37.37; H, 2.84; N, 1.91; Cl, 24.10. IR (KBr, Nujol): ν(CO) 2090 cm^{-1}.

Reaction of 2 with Bromine. To a diethyl ether solution (100 mL) of **2** (0.090 g, 0.144 mmol) was added a solution of bromine in the same solvent dropwise. An orange precipitate was immediately formed. It was filtered, washed with diethyl ether, and dried to give $[(\eta^5\text{-}C_5H_5)Br_2Rh(\mu\text{-}Ph_2PPy)Rh(CO)Br_3]$ (**6**) (0.113 g, 0.118 mmol) in 82% yield. Anal. Calcd for $C_{23}H_{19}Br_5NOPRh_2$: C, 28.70; H, 2.09; N, 1.45; Br, 42.06. Found: C, 28.75; H, 2.12; N, 1.48; Br, 42.11. IR (KBr, Nujol): ν(CO) 2080 cm^{-1}.

Reaction of 2 with Iodine. Procedure a. A diethyl ether solution (20 mL) of iodine (0.028 g, 0.112 mmol) was added dropwise to a solution of **2** (0.070 g, 0.112 mmol) in the same solvent (60 mL). Immediately a brown powder, containing both the products $[(\eta^5\text{-}C_5H_5)Rh(\mu\text{-}I)(\mu\text{-}Ph_2PPy)Rh(CO)I_2]$ (**7**) and $[(\eta^5\text{-}C_5H_5)I_2Rh(\mu\text{-}Ph_2PPy)Rh(CO)I_3]$ (**8**), precipitated. The powder was filtered and extracted with benzene, and 20 mL of heptane was added. On standing, from the solution compound **7** precipitated as dark green microcrystals; yield 0.026 g (0.028 mmol), 25%. After the solvent was removed under reduced pressure, compound **8** was obtained from the mother liquor as a dark red solid, yield 0.054 g (0.045 mmol), 40%. Anal. Calcd for $C_{23}H_{19}I_3NOPRh_2$ (**7**): C, 29.29; H, 2.03; N, 1.48; I, 40.38. Found: C, 29.31; H, 2.08; N, 1.50; I, 40.52. IR (KBr, Nujol): ν(CO) 2020 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.47 (dd, $^2J_{RhH} = 0.6$, $^3J_{PH} = 1.66$ Hz, C_5H_5). Anal. Calcd for $C_{23}H_{19}I_5NOPRh_2$ (**8**): C, 23.08; H, 1.60; N, 1.17; I, 53.02. Found: C, 23.11; H, 1.72; N, 1.20; I, 53.40. IR (KBr, Nujol): ν(CO) 2060 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.54 (dd, $^2J_{RhH} = 0.60$, $^3J_{PH} = 2.19$ Hz, C_5H_5).

Procedure b. The addition of a dichloromethane solution (20 mL) of iodine (0.097 g, 0.382 mmol) to a stirred solution of **2** (0.120 g, 0.191 mmol) in the same solvent (60 mL) soon resulted in a color change from red-brown to dark red. A black residue containing metal-decomposition products was also formed. The solution was filtered and reduced in volume to ca. 30 mL, and diethyl ether (40 mL) was added. By slow evaporation of the solvent compound **8** was obtained as dark red crystals (0.149 g, 0.124 mmol) in 65% yield.

Reaction of 7 with Iodine. A dichloromethane solution (20 mL) of iodine (0.022 g, 0.087 mmol) was added to a solution of **7** (0.082 g, 0.087 mmol) in the same solvent (50 mL). The color of the solution changed from green to dark red while a black residue, containing metal decomposition products, was formed. The solution was filtered and reduced in volume to ca. 20 mL and *n*-hexane (30 mL) added. The solvent was then removed in vacuo to give a dark red solid identified by analytical and spectroscopic data as **8**.

Reaction of 2 with CH_2I_2. A dichloromethane solution (30 mL) of **2** (0.100 g, 0.159 mmol) was treated with 2 mL of CH_2I_2, and the reaction mixture was stirred for 24 h. During this time the reaction course was followed by IR and NMR spectra. The solution was then filtered and the solvent evaporated. The residue, analyzed by IR and NMR spectra, was shown to be a mixture of **7** and **8**. It was dissolved in 5 mL of dichloromethane and transferred onto a neutral alumina column (2 × 20 cm) saturated with diethyl ether. Elution with dichloromethane–diethyl ether (1:1) gave a green fraction from which, on slow evaporation of the solvent, compound **7** precipitated; yield 0.090 g (0.954 mmol), 60%. A red fraction containing compound **8** was obtained by elution with dichloromethane. Removal of the solvent in vacuo afforded **8** (0.029 g, 0.0238 mmol), in 15% yield.

Attempted Reaction of 2 with CH_3I. Compound **2** (0.080 g, 0.127 mmol) was dissolved in dichloromethane (30 mL), and 1 mL of CH_3I was added. The resulting mixture was stirred for 5 h at room temperature. On monitoring the reaction by IR spectroscopy, the disappearance of ν(CO) of the starting material and formation of two new ν(CO) bands at 2030 and 1680 cm^{-1} were observed. The residue obtained by removing of the volatiles was shown to be a mixture of inseparable compounds. The same results were obtained also when the reactions were carried out in different solvents or at lower temperature (0 °C).

X-ray Data Collection and Structure Refinement for 2 and 7. Diffraction measurements for **2** and **7** were made on a Siemens-Stoe four-circle diffractometer using graphite-monochromated Mo Kα ($\lambda = 0.71069$ Å) radiation. Accurate unit-cell dimensions and crystal orientation matrices were obtained from least-squares refinement of 2θ, ω, χ, and ψ values of 20 strong reflections in the range $15° < 2\theta < 28°$ for both compounds. During the course of the intensity data collection the crystals showed no loss in intensity. Crystallographic data and other pertinent information are summarized in Table I. Lorentz and polarization corrections were applied to the data sets. For **7** the absorption correction was made by using an empirical method based on ψ scans (ψ = 0–360° every 10°) for χ values near 90°. Both the structures were solved by using standard Patterson methods, successive least-squares refinements, and difference Fourier maps. Anisotropic temperature factors were introduced for all non-hydrogen atoms except those belonging to the cyclopentadienyl rings in compound **7**; these were refined isotropically. Hydrogen atoms were added at calculated positions and included in the structure factor calculations with a common thermal parameter ($U = 0.08$ Å^2). The weighting scheme used in the last refinement cycles was $w = 0.5222/(\sigma^2(F_o) + 0.001\,725(F_o^2))$ for **2** and $w = 0.9482/(\sigma^2(F_o) + 0.001\,832(F_o^2))$ for **7**, which showed reasonable consistency in a test of $w\Delta^2$ for data sectioned with respect to both F_o and $(\sin\theta)/\lambda$. Both the models reached convergence with $R = [\sum|F_o| - |F_c|]/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ having the values listed in Table I. Scattering factors for non-hydrogen atoms were taken from ref 40 and for hydrogen atoms from ref 41. Anomalous dispersion corrections for Rh, P, Cl, and I atoms were taken from ref 42. All calculations were performed with SHELX76[43] and PARST[44] set of programs on the IBM 4341 computer at the "Centro di Calcolo dell'Universitá di Messina". The refined structures were plotted with use of the ORTEP programs (Figures 1 and 2, respectively). Hydrogen and non-hydrogen coordinates, anisotropic temperature factors, and calculated and observed structure factors are available as supplementary material.

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Registry No. **1**, 119326-22-6; **2**, 119326-23-7; **3**, 119326-24-8; **4**, 119336-07-1; **5**, 119326-25-9; **6**, 119326-26-0; **7**, 119326-27-1; **8**, 119326-28-2; $[Rh(\eta^5\text{-}C_5H_5)(CO)_2]$, 12192-97-1; $[Rh(CO)_2Cl]_2$, 14523-22-9; $[Ir(CO)_2(p\text{-toluidine})Cl]$, 14243-22-2; CH_2I_2, 75-11-6; CH_3I, 74-88-4.

Supplementary Material Available: Tables of atomic coordinates and anisotropic and isotropic thermal parameters (8 pages); listings of observed and calculated structure factors (44 pages). Ordering information is given on any current masthead page.

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