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Characterization of Organometallic Products from the Photochemical Reaction of *trans*-$Rh(PMe_3)_2(CO)Cl$ with Benzene

Sue E. Boyd, Leslie D. Field,* and Martin G. Partridge

Contribution from the Department of Organic Chemistry, University of Sydney, Sydney, NSW 2006, Australia

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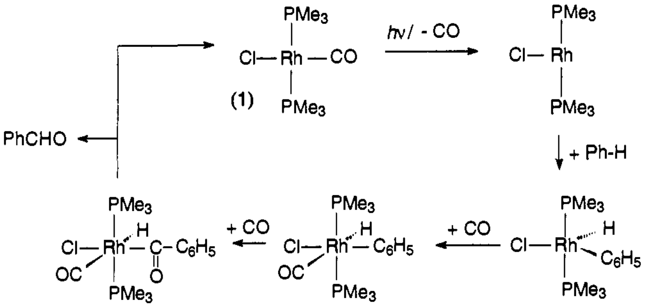
Abstract: Irradiation of *trans*-$Rh(PMe_3)_2(CO)Cl$ (**1**) in benzene/THF (1:3 v/v) at 230 K in the absence of CO affords three main products $Rh(PMe_3)_2(CO)(Cl)(Ph)H$ (two stereoisomers) (**2** and **3**) and *trans*-$Rh(PMe_3)_2(CO)Ph$ (**4**). Both **2** and **3** have phenyl and hydride groups *cis* and **2** has phenyl *trans* to CO. All three products revert to **1** (thermally) if the reaction mixture is allowed to warm to room temperature. The arylrhodium compound **4** is formed by elimination of HCl from one (or both) of the isomeric rhodium(III) compounds **2** and **3**. The arylrhodium complexes **4** and **2** were identified conclusively by independent synthesis and all compounds were fully characterized by NMR techniques. *trans*-$Rh(PMe_3)_2(CO)Ph$ (**4**) reacts with HCl to give only **2**. *trans*-$Rh(PMe_3)_2(CO)Ph$ (**4**) reacts thermally with CO to generate $Rh(PMe_3)_2(CO)_2(COPh)$ (**5**). Under an atmosphere of CO, *trans*-$Rh(PMe_3)_2(CO)Ph$ (**4**) reacts photochemically with benzene to produce benzaldehyde, biphenyl, and benzophenone. The thermal decomposition of a mixture of **2** and **3** formed at low temperature was followed by $^{31}P\{^1H\}$ NMR at several temperatures and kinetic parameters for the process were obtained. Although **2** decomposes directly to **1**, the dominant pathway by which **3** decomposes is by initial isomerization to **2**. For the isomerization of **3** to **2**, $\Delta H^{\ddagger} = 94 \pm 9$ kJ mol^{-1} and $\Delta S^{\ddagger} = +50 \pm 36$ J mol^{-1} K^{-1}. For the decomposition of **2** to **1**, $\Delta H^{\ddagger} = 65 \pm 9$ kJ mol^{-1} and $\Delta S^{\ddagger} = -57 \pm 37$ J mol^{-1} K^{-1}.

The photoactive rhodium(I) complexes $Rh(PR_3)_2(CO)Cl$ (R = aryl, alkyl) are among the most efficient reagents for the catalytic activation and functionalization of hydrocarbons.[1,2] In particular, *trans*-chlorocarbonylbis(trimethylphosphine)rhodium(I), (**1**) reacts with both linear and branched alkanes to give organorhodium complexes which eventually form organic products, *e.g.* by carbonylation or dehydrogenation.[2]

The generally accepted mechanism for carbonylation of organic compounds by **1** involves photochemical loss of CO to form a reactive three-coordinate Rh(I) species which oxidatively adds the C–H bond of an organic substrate.[2c] Addition of CO then forms a 6-coordinate Rh(III) species where migration of the organic group from metal to CO leads to an acylrhodium compound from which the carbonylated product can be eliminated (Scheme 1).

Scheme 1



Ford *et al.*[3] have established the presence of the three-coordinate Rh(I) complex in the reaction mixture in flash photolysis studies of **1** in benzene. Goldman *et al.*[4] have independently synthesized the 6-coordinate acylcarbonyl species $Rh(PMe_3)_2(CO)(Cl)(PhCO)H$ and demonstrated that it is converted to benzaldehyde and **1**. Additionally, in a series of elegant experiments, Goldman *et al.*[4] have measured the quantum yield and wavelength dependence of the photoreaction of **1** with benzene and concluded that the reaction sequence must involve a number of photochemical steps.

At best, the reaction sequence outlined in Scheme 1 is a simplification because, among the reaction byproducts, biphenyl, benzophenone, and benzyl alcohol are formed in significant amounts and these cannot easily be rationalized by Scheme 1 alone. In this paper we report the identification and characterization of some of the major organometallic compounds formed during the course of the photochemical reaction of **1** with aromatic hydrocarbons as well as kinetic parameters for their rearrangement and decomposition. Our results, in combination with those of Goldman *et al.*,[4] allow refinement of the mechanism of C–H activation by $Rh(PMe_3)_2(CO)Cl$ and rationalize the formation of some of the byproducts observed in the photocarbonylation of benzene.

Results and Discussion

The ^{31}P NMR spectrum of a reaction mixture in which *trans*-$Rh(PMe_3)_2(CO)Cl$ (**1**) (125 mM) was irradiated in a mixture of benzene/THF (1:3 v/v) at 230 K under an N_2 atmosphere, *i.e.* in the absence of CO, showed three main products (Figure 1). When the experiment was performed using $Rh(PMe_3)_2(^{13}CO)Cl$ (**1-^{13}C**), all three of the major products have ^{31}P resonances which show an additional coupling to ^{13}C. The three major products have been identified as $Rh(PMe_3)_2(CO)(Cl)(Ph)H$ (two

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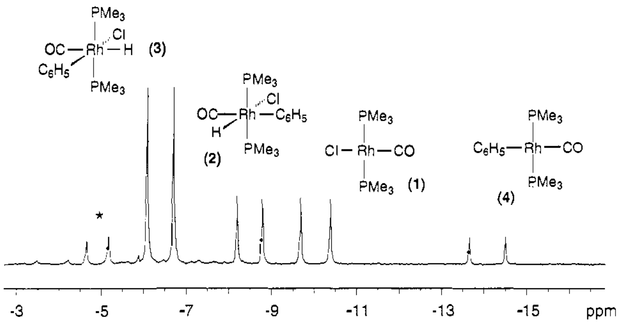
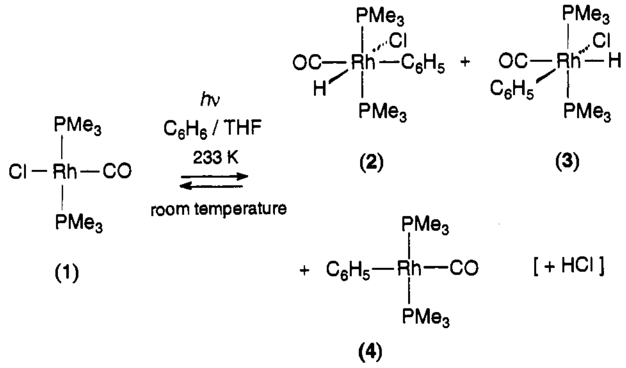


Figure 1. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum (162 MHz, 230 K) of the product mixtures resulting from the irradiation of **1** in a benzene/THF (1:3 v/v) mixture at 230 K for 48 h. The product marked with an asterisk is as yet unidentified.[6]

Scheme 2



stereoisomers, **2** and **3**) and *trans*-Rh(PMe_3)$_2$(CO)Ph (**4**). Both **2** and **3** have phenyl and hydride groups *cis* and **2** has the phenyl substituent *trans* to CO. Under the reaction conditions, mixtures typically contained the products **2**, **3**, and **4** in the approximate ratio 3:8:1 with compounds **1**–**4** accounting for more than 85% of the organometallic products visible in the ^{31}P NMR spectrum.[5] The relative concentration of **4** increased with prolonged periods of irradiation.

On warming a reaction mixture containing **1**, **2**, **3**, and **4** to room temperature, **1** is reformed almost quantitatively (Scheme 2). The quantitative recovery of the starting complex **1** on warming the reaction mixture was independent of the atmosphere (CO or N_2) above the solution.

When the irradiation is carried out under 1 atm of CO there is little change in the $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum for **1**, **2**, or **3** except that the resonances for **1** are broadened and shifted to lower field and this is probably due to exchange with Rh(PMe_3)$_2$(CO)$_2$Cl.[7] The doublet for complex **4** is not observed because it reacts rapidly with CO (*vide infra*). Complexes **2** and **4** have been synthesized and characterized independently.[8]

Complex **4** arises by the elimination of HCl from **2** and/or **3**. When **4** was synthesized independently, the addition of HCl to **4** at low temperature (230 K) generated only **2**[8] with no evidence for the formation of complex **3**. The product formed contains the hydride and chloride ligand *trans* to one another, suggesting a stepwise addition of HCl; in the analogous reaction of Ir(PEt_3)$_2$(CO)(C_6H_5) with HBr, the complex formed contains mutually *trans* hydride and bromide ligands.[9] There is good precedent for the oxidative addition of HX (where X = Cl, Br) to 4-coordinate rhodium and iridium complexes.[10]

Irradiation of **1** in toluene at 230 K results in a similar ^{31}P NMR spectrum to that obtained in benzene/THF except that there are several resonances grouped with chemical shifts similar to each of **2**–**4** resulting from the formation of positional isomers. Irradiation of **1** in mesitylene produces almost exclusively the 4-coordinate mesityl arylrhodium analogue of **4**.[11]

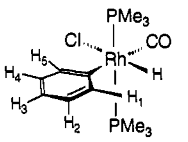
NMR Spectroscopy

Rhodium(I) and rhodium(III) products formed in the reaction mixture were characterized by ^{31}P, ^{1}H, and ^{13}C NMR spectroscopy. Selected NMR data are given in Table 1.

^{31}P NMR Spectroscopy. The $^{31}\mathrm{P}\{^1\mathrm{H}\}$ resonance of the starting material *trans*-Rh(PMe_3)$_2$(CO)Cl (**1**) appears at δ −10.03 as a rhodium-coupled doublet ($^1J_{\mathrm{Rh-P}}$ = 114.7 Hz). On irradiation at 230 K in a benzene/THF (1:3 v/v) mixture, the resonance of the starting material is depleted with the concomitant increase in the signals of **2**, **3**, and **4**. The $^{31}\mathrm{P}\{^1\mathrm{H}\}$ resonance of *trans*-Rh(PMe_3)$_2$(CO)Ph (**4**) occurs to high field of the starting material **1** (at δ −14.13) as a rhodium-coupled doublet ($^1J_{\mathrm{Rh-P}}$ = 137.2 Hz). The ^{31}P resonances of **2** and **3** appear at δ −8.53 ($^1J_{\mathrm{Rh-P}}$ = 98.4 Hz) and δ −6.55 ($^1J_{\mathrm{Rh-P}}$ = 100.4 Hz), respectively. In addition, the ^{31}P resonances of another minor product (total concentration < 10%) appears as rhodium-coupled doublet (δ −5.47 ppm) and the compound giving rise to this signal has yet to be identified.[6]

^{1}H NMR Spectroscopy. Resonances of two groups of metal hydrides are observed in the high-field region of the ^{1}H NMR (230 K) spectrum after *trans*-Rh(PMe_3)$_2$(CO)Cl (**1**) has been irradiated in a benzene/THF solution. The hydride of complex **3** appears at δ −8.05 as a doublet of triplets with $^1J_{\mathrm{Rh-H}}$ = 13.2 Hz and $^2J_{\mathrm{P-H}}$ = 13.2 Hz and the hydride of complex **2** appears at δ −14.62 as a doublet of triplets with $^1J_{\mathrm{Rh-H}}$ = 28.1 Hz and $^2J_{\mathrm{P-H}}$ = 13.9 Hz (Figure 2).

The low-field region of the ^{1}H NMR spectrum shows resonances due to several PMe_3 groups in the normal aliphatic range near δ 1.5 ppm. The aryl resonances of complexes **2**, **3**, and **4** appear in the region δ 8.4 to δ 6.8 and the 5-spin systems observed for the aryl groups of **2** and **3** indicate that each complex has an η^1-coordinated phenyl ligand. For the complexes **2** and **3**, five nonequivalent proton resonances are observed for the phenyl groups indicating restriction of the rotation of the monosubstituted benzene rings about the Rh–arene bond (on the NMR time scale at 400 MHz at 230 K). The aromatic region of the ^{1}H NMR spectrum is complicated by the overlap of signals from aryl rings from the mixture of products. The assignment of the aliphatic, aromatic, and hydride resonances of **2**, **3**, and **4** was accomplished with a combination of COSY, TOCSY, and NOESY experiments.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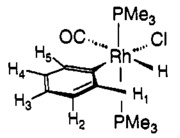
(3)

The ^{1}H NOESY spectrum of a reaction mixture where **1** was irradiated in a dilute solution of benzene in THF-d_8 (1:9 v/v) for 108 h at 230 K showed strong cross peaks between protons of the

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(5) Irradiation of **1** in the presence of aromatic substrates is reliable and reproducible. We have examined the system in more than 60 independent irradiation experiments, the data reported here are from a "typical" experiment.

(6) Under the irradiation conditions, a minor product at δ ^{31}P (THF-d_8, 230 K) −5.47 ppm ($^1J_{\mathrm{Rh-P}}$ = 110 Hz) is formed (ca. 5–10% of the product mixture). This product is formed when **1** is irradiated in THF alone and presumably arises from activation of the THF solvent or by dimerization of **1**.

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(11) NMR data (ppm) for Rh(PMe_3)$_2$(CO)(mesityl): δ ^{31}P (THF-d_8, 230 K) −12.56 ($^1J_{\mathrm{Rh-P}}$ = 138 Hz); δ ^{1}H (THF-d_8, 230 K) 6.61 (s, 2H, 2 × Ar-H), 2.42 (s, 6H, 2 × 2,6-Ar-Me), 2.22 (s, 3H, 1 × 4-Ar-Me), 1.34 (m, 18H, 2 × PMe_3).

Table 1. Selected ^{31}P, ^{1}H, and ^{13}C NMR Data for Complexes **2**, **3**, **4** and **5**[a]

	^{1}H NMR		^{31}P{^{1}H}		^{13}C{^{1}H}[c]	
complex	δ/ppm (J/Hz)[b]	assign	δ/ppm (J/Hz)[b]	assign	δ/ppm (J/Hz)[b]	assign
2	8.28 (d, $^{3}J_{5,4}$ = 8.6)	H^5	−8.53 (d, $^{1}J_{RhP}$ = 98.4)	PMe_3	190.94 (dt, $^{1}J_{RhC}$ = 43.3, $^{2}J_{PC}$ = 9.6)	Rh–CO
	7.4 (masked)	H^1				
	7.10–7.04 (m)	H^4				
	7.00–6.93 (m)	$H^{2,3}$				
	1.36 (m)	PMe_3				
	−14.62 (dt, $^{1}J_{RhH}$ = 28.1 $^{2}J_{PH}$ = 13.9, $^{2}J_{HC}$ = 4.7)	Rh–H				
3	7.32 (d, $^{3}J_{5,4}$ = 7.5)	H^1	−6.55 (d, $^{1}J_{RhP}$ = 100.4)	PMe_3	191.60 (dt, $^{1}J_{RhC}$ = 42.7, $^{2}J_{PC}$ = 9.0)	Rh–CO
	7.27 (d, $^{3}J_{1,2}$ = 6.9)	H^5				
	6.93–6.86 (m)	$H^{2,3,4}$				
	1.46 (m)	PMe_3				
	−8.05 (dt, $^{1}J_{RhH}$ = 13.2, $^{2}J_{PH}$ = 13.2, $^{2}J_{HC}$ = 65)	Rh–H				
4	7.28 (m)	$H^{1,5}$	−14.13 (d, $^{1}J_{RhP}$ = 137.2)	PMe_3	198.0(dt, $^{1}J_{RhC}$ = 55.4, $^{2}J_{PC}$ = 14.0)	Rh–CO
	6.98 (m)	$H^{2,4}$			175.5 (dt, $^{1}J_{RhC}$ = 26.6, $^{2}J_{PC}$ = 16.8)	C_{ipso}
	6.83 (m)	H^3			140.2 (t, $^{3}J_{Cp}$ = 3.6)	C^2
	1.32 (m)	PMe_3			127.7 (s)	C^3
					123.5 (s)	C^4
					17.8 (m)	PMe_3
5	7.97 (m)	$H^{1,5}$	−14.80 (dd, $^{1}J_{RhP}$ = 73, $^{2}J_{PP}$ = 39 Hz)		242.3 (dd, J = 86, 20)	(C(O)Ph)
	7.44 (m)	$H^{2,3,4}$	−30.30 (dd, $^{1}J_{RhP}$ = 142, $^{2}J_{PP}$ = 39 Hz)		200.6 (t, J = 19.2)	Rh–CO
	1.63 (br)	PMe_3				
	1.53 (br)	PMe_3				

[a] NMR data were recorded at 230 K. Data for complexes **2** and **3** were recorded in benzene/THF (1:9 v/v) mixtures, and data for **4** and **5** were recorded in THF-d_8. [b] The signs of the coupling constants are not implied. [c] Couplings to ^{13}C obtained from ^{13}CO enriched samples.

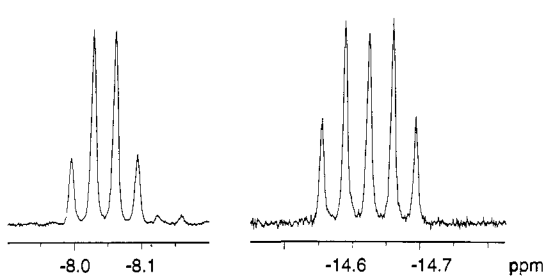

Figure 2. Sections of the high-field region of the ^{1}H NMR spectrum (400 MHz, 230 K) of the product mixture resulting from the irradiation of Rh(PMe$_3$)$_2$(CO)Cl (**1**) in a benzene/THF (1:3 v/v) mixture at 230 K for 48 h. There are no other resonances for metal-bound hydrides in this spectrum.

PMe$_3$ ligands and *ortho* protons on the phenyl ligands. Strong cross peaks were also observed between the resonances of the metal-bound hydride nuclei of both **2** and **3** and the PMe groups. The methyl protons of the PMe$_3$ groups of complex **2** show a strong interaction with two aromatic protons (δ 8.28 and 7.4 ppm) and the metal hydride shows a cross peak only with the proton at δ 7.4. This establishes the stereochemistry of **2** such that the metal-bound hydride and the aromatic ring occupy adjacent (mutually *cis*) coordination sites and further identifies and assigns the aromatic proton spin system of **2**.

The NOESY spectrum of **3** showed enhancements between the resonances of the metal-bound hydride (δ −8.05 ppm), the corresponding PMe$_3$ resonance (δ 1.46 ppm), and a proton in the aromatic region at δ 7.32 ppm. The PMe$_3$ resonances showed strong NOESY enhancement of the aromatic protons at δ 7.32 and 7.27 ppm. This again establishes that the metal-bound hydride and aromatic ring in **3** occupy adjacent coordination sites on Rh. (Figure 3) as in complex **2**.

^{13}CO Labeling and ^{13}C NMR Spectra. ^{13}CO-labeled *trans*-Rh(PMe$_3$)$_2$(^{13}CO)Cl (**1**-^{13}**CO**) was used to confirm the presence of CO in the irradiation products, and the magnitude of the C–P and C–H coupling constants positions the CO substituent in the rhodium coordination sphere. The ^{31}P{^{1}H} NMR spectrum recorded after a sample of **1–^{13}CO** has been irradiated in a benzene/THF (1:3 v/v) mixture at 230 K for 48 h showed each of the resonances assigned to complexes **2**, **3**, and **4** had an additional coupling ($^{2}J_{P-C}$ = 8–16 Hz). Similarly the resonances of the metal-bound hydrides of **2** and **3** show an additional splitting due to ^{13}C–^{1}H coupling (Table 1).

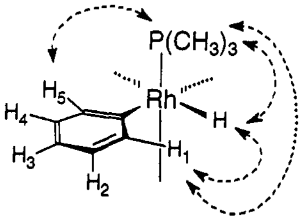

Figure 3. Schematic indicating nuclei where important strong interproton NOESY interactions are detected in **2** and **3**.

The hydride resonances were paired with their respective carbonyl resonances using selective ^{1}H detected ^{13}C X-H correlation spectra.[12,13] The hydride resonance of complex **3** has a $^{2}J_{H-C}$ coupling of about 65 Hz and that of complex **2** has a corresponding coupling of 4.7 Hz.[12] The relatively large magnitude of the coupling ($^{2}J_{H-C}$) observed in the hydride resonance of **3** indicates that the hydride ligand occupies a coordination site *trans* to the ^{13}CO ligand.[14] The chemical shift of the resonance (δ −8.05) further supports the assignment of the hydride *trans* to a CO ligand.[15] The metal carbonyl region of the ^{13}C{^{1}H} NMR spectrum of the ^{13}CO-enriched products shows a series of rhodium- and phosphorus-coupled resonances. All have the characteristic doublet of triplet multiplicity as expected for ^{13}C with coupling to rhodium and two equivalent ^{31}P nuclei.

The Role of Rh(PMe$_3$)$_2$(CO)Ph (4). When Rh(PMe$_3$)$_2$(CO)Ph (**4**) is irradiated in benzene solution under an atmosphere of CO, benzaldehyde is formed. Since **4** is produced as an organometallic product when **1** is irradiated in benzene, at least some of the benzaldehyde (as well as other products) could arise by secondary carbonylation reactions with **4**. The addition of CO to a THF solution (240 K) of *trans*-Rh(PMe$_3$)$_2$(CO)Ph (**4**) immediately forms the 5-coordinate benzoylrhodium complex

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[12] Selective ^{1}H–^{13}C correlation experiments indicate that $^{2}J_{C-Rh-H}$(*cis*) is of opposite sign to $^{2}J_{C-Rh-H}$(*trans*): Field, L. D.; Messerle, B. A.; Partridge, M. G. Unpublished results.

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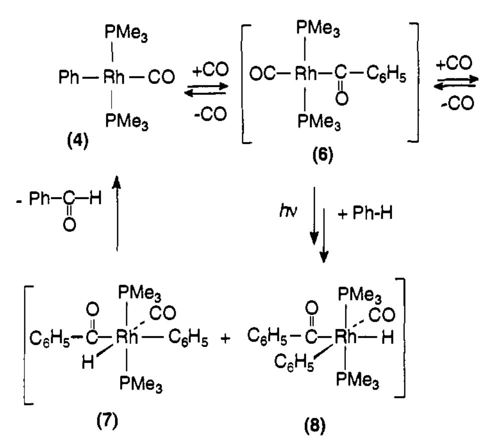
[14] See for example: (a) Whitesides, G. M.; Maglio, G. *J. Am. Chem. Soc.* **1969**, *91*, 4980. (b) Brown, J. M.; Kent, A. G. *J. Chem. Soc., Perkin Trans. II* **1987**, 1597.

[15] Moore, D. S.; Robinson, S. D. *Chem. Soc. Rev.* **1983**, *12*, 415.

Scheme 3



$Rh(PMe_3)_2(CO)_2(COPh)$ (5).[16] The $^{31}P\{^1H\}$ NMR spectrum of 5 appears as two resonances at δ −14.80 (dd, $^1J_{Rh-P}$ = 73, $^2J_{P-P}$ = 39 Hz) and δ −30.30 (dd, $^1J_{Rh-P}$ = 142 Hz, $^2J_{P-P}$ = 39 Hz) indicating that the stereochemistry of the complex has the PMe_3 ligands *cis*, however saturation transer experiments indicate that the complex is fluxional on the NMR time scale at 230 K. .

Irradiation of a sample of 4 (9.3 mM in 2 mL of benzene) for 16 h at room temperature under a CO atmosphere[17] afforded benzaldehyde, biphenyl, and benzophenone (confirmed by GC/MS).[18] Goldman *et al.*[4] have confirmed that the amount of benzaldehyde generated by irradiation of 4 under CO in benzene is significantly less than that produced by irradiation of 1 under the same conditions. The organic products are formed only when the mixture is irradiated and these are presumably the result of the photochemical reaction of complex 6 with benzene (Scheme 3).

Although the 6-coordinate benzoylrhodium species have not been observed directly, reductive elimination of either benzaldehyde or benzophenone is clearly possible from these species. Biphenyl could arise from the direct photochemical addition of 4 to benzene. Subsequent elimination of biphenyl would form *trans*-$Rh(PMe_3)_2(CO)H$,[19] however biphenyl is detected only in trace amounts when 4 is irradiated under N_2 in benzene.[20] In the presence of CO, it is not unreasonable that biphenyl could be derived from an alternative pathway involving phenyl migration from the benzoyl carbon to rhodium in 7 and 8 with loss of CO to form $Rh(PMe_3)_2(Ph)(Ph)(CO)(H)$ from which reductive elimination of biphenyl would also give *trans*-$Rh(PMe_3)_2(CO)H$.

Kinetic Studies of the Thermal Decomposition of $Rh(PMe_3)_2(CO)(Cl)(Ph)H$. The addition of HCl to an authentic sample of 4 at low temperature generates only complex 2. On warming a solution of 2 to room temperature (in the presence of excess HCl), the complex decays thermally to 1. There is no evidence for the formation of 3 or other isomers of $Rh(PMe_3)_2(Ph)(H)(CO)Cl$. In a reaction mixture containing excess HCl, 1 reacts immediately to form $Rh(PMe_3)_2(CO)(Cl)_2H$.[8] At 260 K, complex 2 has a half-life of 12.3 min.

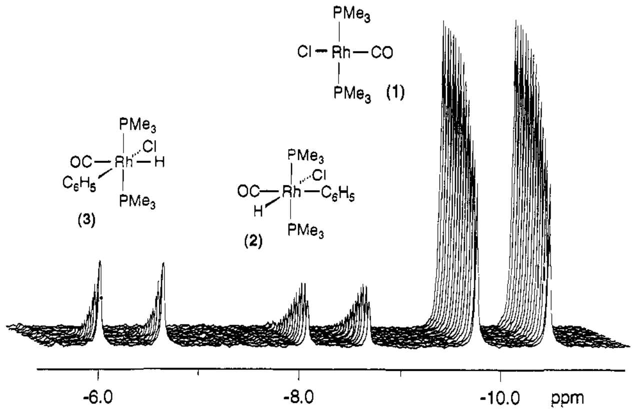
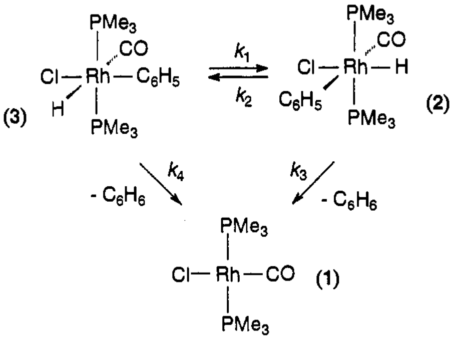


Figure 4. ^{31}P spectra showing the thermal decomposition of 2 and 3 to 1 as a function of time (162 MHz, 268 K, benzene/THF 1:3). Sixteen spectra were collected at intervals of 4.28 mins.

Scheme 4



Both 2 and 3 are thermally converted to (1) if the temperature of a reaction mixture is raised above 250 K. Both 2 and 3 have phenyl and hydride ligands *cis* at the metal center, and in principle, the direct reductive elimination of benzene to form 1 could occur from both isomers ($2 \rightarrow 1 \leftarrow 3$).

A mixture containing 1, 2, 3, and 4 was prepared by irradiation of 1 (125 mM, 0.5 mL) in a benzene/THF (1:3 v/v) mixture at 230 K for 48 h. The sample was placed in the pre-cooled probe of an NMR spectrometer and $^{31}P\{^1H\}$ spectra were recorded automatically over a period. A typical time course of the reaction (Figure 4) shows that both 2 and 3 diminish with time as the concentration of 1 increases at 268 K. The concentration of *trans*-$Rh(PMe_3)_2(CO)Ph$ (4) as well as minor products in the reaction mixture remains essentially constant throughout the course of the reaction at this temperature.

From the qualitative shape of the profile (Figure 4) it is apparent that the decay of 2 to 1 is not a simple first-order exponential process. In particular, there is an obvious initial lag time where the concentration of 2 increases before its concentration decreases. This suggests that there is an interconversion between 2 and 3 at a rate comparable to the elimination of C_6H_6.

The data for the thermal decomposition of 2 and 3 to form 1 at several temperatures was fitted to a kinetic scheme incorporating interconversion of 2 and 3 (Scheme 4, and Figure 5). In all cases k_2 and k_4 were too small (compared to the magnitude of k_1 and k_3) to be measured reliably (Table 2). The rate of isomerization of 3 to 2 and decomposition of 2 to 1 is independent of the gas in the solution (N_2 or CO).[21]

The decay of isomer 2 to compound 1 is much faster than the direct decay of 3 to 1. The dominant pathway by which 3 converts to 1 is by the initial isomerization to 2 which then decays relatively rapidly to 1. From the data in Tabl3 2, the activation parameters for isomerization $3 \rightarrow 2$ are $\Delta H^\ddagger$ = 94 ± 9 kJ mol^{-1} and $\Delta S^\ddagger$ =

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[16] Related rhodium and iridium complexes have been characterized previously. See for example: (a) Yagupsky, G.; Brown, C. K.; Wilkinson, G. *J. Chem. Soc. A* **1970**, 1392. (b) Rees, W. M.; Churchill, M. R.; Li, Y.-J.; Atwood, J. D. *Organometallics* **1985**, *4*, 1162. (c) Deutsch, P. P.; Eisenberg, R. *Organometallics* **1990**, *9*, 709. (d) Cleary, B. P.; Eisenberg, R. *Organometallics* **1992**, *11*, 2335. (e) Brown, J. M.; Kent, A. G. *J. Chem. Soc., Chem. Commun.* **1982**, 723. (f) See also ref *1a*.

[17] 4 was irradiated in a quartz cuvette with a cut-off filter ($\lambda > 295$ nm) under an atmosphere of CO (1 atm) with a 200 W medium pressure mercury vapor lamp for 16 h at 283 K.

[18] Benzaldehyde, biphenyl, and benzophenone were formed in the approximate ratio 10:1:20; total yield of benzaldehyde 80 μmol, 4.3 turnovers.

[19] Similar intermediates have been proposed in related iridium chemistry. See for example: (a) Johnson, C. E.; Fisher, B. J.; Eisenberg, R. *J. Am. Chem. Soc.* **1983**, *105*, 7772. (b) See also ref *1b*.

[20] Irradiation of 4 in a mixture of THF/benzene-d_6 (3:1) at 233 K for 68 h under 1 atm of N_2 affords D_5H_5 biphenyl (detected and characterized by GC/MS).

[21] Under N_2 at 268 K, k_1 = (1.13 ± 0.09) × 10^{-3} s^{-1} and k_3 = (1.44 ± 0.09) × 10^{-3} s^{-1}. Under CO at 268K, k_1 = (1.05 ± 0.04) × 10^{-3} s^{-1} and k_3 = (1.50 ± 0.05) × 10^{-3} s^{-1}.

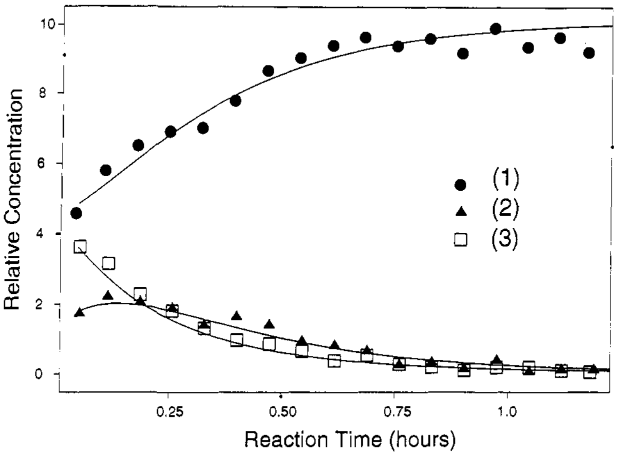

Figure 5. Plot of the relative concentrations of **1**, **2**, and **3** as a function of time (268 K). The solid lines represent the curves of best fit according to Scheme 4 with $k_1 = 1.13 \times 10^{-3}$ s^{-1}, $k_3 = 1.44 \times 10^{-3}$ s^{-1}, and $k_2 = k_4 = 0$.

Table 2. Rate Constants for the Isomerization and Decomposition of **2** and **3** according to Scheme 4[a]

temp[b]	k_1 (s^{-1})	k_3 (s^{-1})
251	$(7.38 \pm 0.3) \times 10^{-5}$	$(2.23 \pm 0.08) \times 10^{-4}$
258	$(1.60 \pm 0.06) \times 10^{-4}$	$(3.48 \pm 0.13) \times 10^{-4}$
263	$(5.84 \pm 0.23) \times 10^{-4}$	$(9.64 \pm 0.37) \times 10^{-4}$
268	$(1.13 \pm 0.09) \times 10^{-3}$	$(1.44 \pm 0.09) \times 10^{-3}$

[a] k_2 and k_4 were too small to be measured independently in this experiment and were taken to be 0.0 s^{-1}. [b] In K ± 1 K.

+ 50 ± 36 J mol^{-1} K. The activation parameters for conversion of **2** → **1** are $\Delta H^{\ddagger} = 65 \pm 9$ kJ mol^{-1} and $\Delta S^{\ddagger} = -56 \pm 35$ J mol^{-1} K^{-1}.[22] The entropy of activation for the isomerization **3** → **2** is positive and this would be consistent with an isomerization mechanism where the transition state was less congested that the six-coordinate complex **3**. The isomerization of **3** to **2** could reasonably occur through an η^2-benzene complex. Isomerization of arylrhodium complexes via η^2-bound arene intermediates is well established in the reaction chemistry of $(C_5R_5)Rh(PMe_3)(aryl)H$ (where R = H or Me).[23]

Experimental Section

General Information. All operations were performed under a nitrogen atmosphere, either on a vacuum line using standard Schlenk methods or in a drybox. Rhodium trichloride was obtained as a generous loan from Johnson Matthey Inc. Trimethylphosphine was obtained from Aldrich Chemicals and used without further purification. Nitrogen (>99.5%), carbon monoxide (>99.5%), and HCl (technical grade) were purchased from CIG-HYTEC. ^{13}CO (99 atom % ^{13}C, 10.5% ^{18}O) was purchased from Isotec Inc. Gases were used without further purification. Pentane, hexane, diethyl ether, THF, benzene, and toluene were distilled under an atmosphere of nitrogen from purple solutions of sodium benzophenone ketyl.

NMR spectra were recorded on Bruker AC200 (^{1}H at 200.13 MHz), AMX400 (^{1}H at 400.13 MHz, ^{31}P at 162.0 MHz, and ^{13}C at 100.6 MHz), and AMX600 (^{1}H at 600.13 MHz,) spectrometers. The probe temperature of the NMR spectrometers was regulated by a Bruker BVT-1000 temperature controller and calibrated against the proton spectrum of methanol.[24] Deuterated solvents, THF-d_8, toluene-d_8, and benzene-d_6 were obtained from Merck and used without further purification.

Low-temperature irradiation experiments (230 K) were carried out using a 125 W medium-pressure mercury vapor lamp. NMR tubes containing samples to be irradiated were suspended in a double-walled Pyrex dewar containing ethanol cooled with a refrigeration coil.

NMR Spectroscopy. NMR data processing was done using Bruker ASPECT-X32 and SUN Sparc station processing facilities using standard Bruker software. In the presentation of NMR data, chemical shifts (δ) are in ppm, the downfield region being positive. ^{1}H and ^{13}C chemical shifts are referenced to residual solvent resonances. ^{31}P chemical shifts are referenced to external, neat trimethyl phosphite, taken as 140.85 ppm at the temperature quoted. Broad-band decoupling of one- and two-dimensional ^{13}C and ^{31}P spectra was achieved with composite pulse decoupling using the WALTZ-16 sequence.[25] Heteronuclear decoupling of one- and two-dimensional ^{1}H and heteronuclear spectra was achieved with composite pulse decoupling using the GARP sequence[26] during the acquisition only. All homonuclear two-dimensional ^{1}H spectra were acquired using ^{31}P decoupling in both dimensions. All homonuclear and heteronuclear two-dimensional NMR experiments were acquired using TPPI.[27] For DQF-COSY[28,29] and TOCSY[29] experiments, sweep widths were contracted to include only the aromatic and aliphatic resonances and 400 increments of 32 transients were acquired. The mixing interval for the TOCSY experiments was 52 ms. Shifted sine bell weighting functions were used in both dimensions prior to Fourier transformation. 2D-NOESY spectra were acquired with 512 increments of 32 transients. Cosine weighting was used prior to Fourier transformation. The mixing interval for 2D-NOESY experiments was 1.4 s. Baseline distortions were removed using a polynomial fit for order 3 for TOCSY and 2D-NOESY spectra. ^{1}H-detected selective H–X correlation experiments used a "top hat" pulse shape for excitation[30] using shaped pulses defined by 256 steps. A pulse length of 15 ms was calibrated to have an effective ^{1}H excitation window of *ca.* 250 Hz. Selective, inverse-detection H–X correlation experiments were acquired with 256 increments of 16 transients.

Synthesis. The preparations of *trans*-$Rh(PMe_3)_2(CO)Cl$ (**1**)[31] and *trans*-$Rh(PMe_3)_2(CO)Ph$[8] have been described previously.

Preparation of ^{13}CO-Enriched $Rh(PMe_3)_2(CO)Cl$ (1-^{13}CO). A solution of **1** (120 mg, 0.38 mmol) in THF (3 mL) was stirred under an atmosphere of ^{13}C-enriched carbon monoxide (50 mL, 1 atm, 5.2 equiv) for 10 min. The solvent was removed under vacuum and the residue crystallized by evaporation of a saturated ether solution at ambient temperature. $^{31}P\{^1H\}$ NMR analysis of solutions of the crystals showed a mixture of ^{12}CO and ^{13}CO isotopomers of complex **1** in a ratio of approximately 1:4.

Irradiation Experiments with 1 in Arenes. Solutions of **1** (125 mM) were prepared either in neat arene (in the case of toluene) or in a solution of arene in THF (10 to 25% v/v) under nitrogen. For protonated solvents, one drop on an appropriate degassed deuterated solvent was added to all samples to provide an internal lock for NMR spectroscopy. The probe of an NMR spectrometer was pre-cooled to the temperature used in the irradiation before the sample was introduced into the spectrometer. Irradiation intervals varied depending on the solvent system. In a typical experiment, a solution of **1** in benzene/THF (1:3 v/v) (125 mM, 0.5 mL) required 48 h of irradiation to achieve *ca.* 80–90% conversion of the starting material. A solution of **1** in neat toluene (125 mM, 0.5 mL) required approximately 4 h of irradiation to achieve *ca.* 80–90% conversion.

Gas- and Solvent-Exchange Experiments. In gas- or solvent-exchange experiments, samples were prepared in 5 mm high-precision NMR tubes sealed with O-ring valves.[32] In samples requiring solvent exchange, the irradiated samples were suspended in a dewar of ethanol cooled to 240 K using refrigeration coil. The tube was connected to a high-vacuum line, the O-ring opened, and the solvent removed under vacuum. Fresh solvent was condensed into the NMR tube.

Kinetic Analyses. The decomposition and isomerization of **2** and **3** were followed quantitative by ^{31}P NMR spectroscopy. Spectra (16 scans, total aquisition time for each spectrum was 1.28 min) were accumulated

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(22) At 298 K, these values extrapolate to $\Delta G^{\ddagger} = 78.9 \pm 2$ kJ mol^{-1} ($k_2 = 0.088$ s^{-1}, $t_{1/2} = 7.9$ s) for the isomerization of **3** to **2** and $\Delta G^{\ddagger} = 81.6 \pm 2$ kJ mol^{-1} ($k_1 = 0.031$ s^{-1}, $t_{1/2} = 22$ s) for the conversion of **2** to **1**.

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(32) Supplied by J. Young (Scientific Glassware) Ltd., UK, Catalog VNMR-5.

automatically at intervals in a spectrometer whose probe temperature had been stabilized. Spectra were automatically integrated and data fitted to kinetic equations describing Scheme 3 using a nonlinear least-squares analysis.

Conclusions

The NMR analysis of solutions of **1** in benzene/THF after irradiation at ≤235 K has enabled the identification of some of the major organometallic products. Two of the product complexes **2** and **3** are isomers of the structural formula $Rh(PMe_3)_2(CO)(Cl)(Ph)H$ in which the PMe_3 ligands occupy mutually *trans* coordination sites and the hydride and aryl ligands mutually *cis* coordination sites. The third major product complex formed in the reaction mixture is *trans*-$Rh(PMe_3)_2(CO)Ph$ (**4**), and this compound arises by the elimination of HCl from one or both of the complexes **2** and **3**.

All three products **2**, **3**, and **4** revert thermally to **1** if the reaction mixture is allowed to warm and the decomposition of a mixture of **2** and **3** afforded kinetic parameters. Although **2** decomposes directly to **1**, the dominant pathway by which **3** decomposes is by initial isomerization to **2**.

In the photochemical reaction of *trans*-$Rh(PMe_3)_2(CO)(Cl)$ with benzene, there are now a number of organometallic compounds that have been detected. *trans*-$Rh(PMe_3)_2(CO)(Ph)$, which is formed in the reaction mixture when *trans*-$Rh(PMe_3)_2(CO)(Cl)$ is irradiated, is itself photochemically active and produces benzaldehyde when irradiated under a CO atmosphere. Similarly although $Rh(PMe_3)_2(CO)(COPh)$ and $Rh(PMe_3)_2(CO)(H)$ have not yet been observed directly, their presence in the reaction mixture is inferred from other species formed and these four-coordinate complexes would be expected to be capable of C–H activation reactions under the normal reaction conditions.

The activation of C–H bonds by $Rh(PMe_3)_2(CO)(Cl)$ is not a simple process. Once the reaction initiates, we now know that there are a number of secondary organometallic species produced which themselves are capable of C–H activation.

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