

# Solution and Nujol Matrix Photochemistry of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Os}_2(\text{CO})_4$ and Nujol Matrix Photochemistry of $(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)_2\text{Ru}_2(\text{CO})_4$ and $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2\text{H}$ , Where M = Ru and Os

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Lowering the temperature of a Nujol solution of  $(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)_2\text{Ru}_2(\text{CO})_4$  containing bands of the *trans*- and *cis*-bridging and *trans*-nonbridging isomers from room temperature to ca. 90 K results in complete disappearance of the bands of the *trans*-terminal isomer. The photochemistry of  $(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)_2\text{Ru}_2(\text{CO})_4$  in frozen Nujol at 90 K differs subtly from that of  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(\text{CO})_4$  in inert gas matrixes at 12 K in that the *trans*-bridging isomer is found to undergo photolysis at high energy ( $\lambda_{\text{irr}} > 250$  nm) to yield both the triply bridged carbonyl-loss species,  $(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)_2\text{Ru}_2(\mu\text{-CO})_3$ , and the *cis*-bridged species isomer. There is no evidence for formation of the *trans*-nonbridged isomer upon photolysis as observed for  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(\text{CO})_4$ . The solution photochemistry of  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Os}_2(\text{CO})_4$  is shown to closely parallel that of  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(\text{CO})_4$ . Photolysis of  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Os}_2(\text{CO})_4$  in  $\text{CHCl}_3$  yields  $(\eta^5\text{-C}_5\text{H}_5)\text{Os}(\text{CO})_2\text{Cl}$ , while photolysis in benzene yields hydride products believed to arise from metal-to-ring coupling of radicals. Photolysis of  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Os}_2(\text{CO})_4$ , which exists only in a nonbridged form, in frozen Nujol (90 K) results in CO loss and formation of  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Os}_2(\mu\text{-CO})_3$  as the only photoproduct. Photolysis of  $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2\text{H}$ , where M = Ru or Os, in frozen Nujol yields  $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})\text{H}$  and a second product that appears to be either  $(\eta^5\text{-C}_5\text{H}_6)\text{M}(\text{CO})_2$  or the  $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2$  radical.

## Introduction

An extensive photochemistry of  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_4$ , **I**, and  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(\text{CO})_4$ , **II**, has been reported. This photochemistry has been reviewed up to 1999.<sup>1,2</sup> Solution, matrix, and time-resolved methods have been used to elucidate the mechanisms of these photoprocesses. For **I** and **II**, reaction manifolds involving both radical and carbonyl-loss intermediates have been established.<sup>3</sup> Photolysis of **I** in solution and in a variety of frozen matrixes at 12 and 90 K has been found to yield a carbonyl-loss product,  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\mu\text{-CO})_3$ .<sup>4</sup> Theoretical studies, confirmed by the isolation of the methylated derivative,  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Fe}_2(\mu\text{-CO})_3$ ,<sup>5</sup> have established

that this species has a triplet ground state. In frozen inert gas matrixes at 12 K, photolysis of **II** results in the formation of an analogous species,  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-CO})_3$ , along with opening of the *trans*-bridged isomeric species to the *trans*-nonbridged isomer.<sup>4c</sup> Preliminary time-resolved IR studies of **II** in solution have observed radical formation, but there was no evidence under these conditions for the triply bridged, CO-loss intermediate.<sup>6</sup> A simple explanation for the absence of CO-loss species in the solution photolyses of **II** may be the known preference of **II** for unbridged conformers in room-temperature solution, while **I** tends to prefer bridged conformations.<sup>7</sup>

Although  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Os}_2(\text{CO})_4$ , **III**, was first reported almost 40 years ago,<sup>8</sup> we were surprised by the complete absence of photochemical studies in the literature. Indeed the only photochemical study of a derivative of **III** appears to be that of Johnson and Baird,<sup>9</sup> who have shown that solution photolysis of  $(\eta^5\text{-C}_5\text{Me}_5)\text{Os}(\text{CO})_2$

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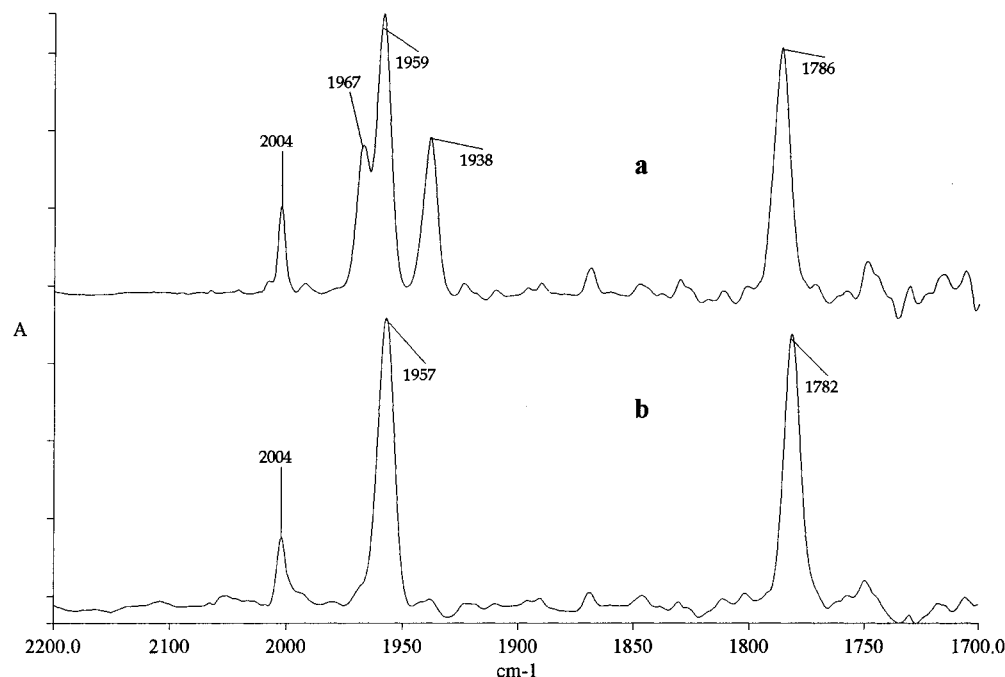
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**Figure 1.** Nujol solutions of  $(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)_2\text{Ru}_2(\text{CO})_4$  at (a) room temperature and (b) ca. 90 K.

$\text{CH}_2\text{Ph}$  in the presence of  $\text{PMe}_2\text{Ph}$  results in the formation of *exo*- $(\eta^4\text{-C}_5\text{Me}_5\text{CH}_2\text{Ph})\text{Os}(\text{CO})_2\text{PMe}_2\text{Ph}$  by what was believed to be a radical mechanism. The paucity of photochemical studies is certainly due to the expense of the osmium starting materials and the difficulties associated with the synthesis of **III** and its derivatives. An excellent modern preparation of **III** reported by Herrmann and co-workers<sup>10</sup> has solved the second of these problems and has opened the way for this introductory study into the photochemistry of **III**. By way of comparison, the photochemistry of  $(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)_2\text{Ru}_2(\text{CO})_4$ , **IV**, in frozen Nujol at ca. 90 K has been carried out.

$(\eta^5\text{-C}_5\text{H}_5)\text{Os}(\text{CO})_2\text{H}$ , **V**, is prepared as an intermediate in the synthesis of **III**,<sup>10</sup> and its ruthenium analogue,  $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2\text{H}$ , **VI**, is readily prepared by reaction of  $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2\text{Cl}$  with  $\text{NaBH}_4$ .<sup>11</sup> Although the photochemistry of the group VI hydrides,  $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{H}$ , where  $\text{M} = \text{Mo}$  and  $\text{W}$ , have been examined in inert gas matrixes,<sup>12</sup> no reports have appeared concerning the photointermediates of **IV**, and only one brief study of **VI** has been reported. In this latter work, **VI** was photolyzed in neat 1-pentene (90 K) with formation of  $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})(1\text{-pentene})\text{H}$ .<sup>13</sup>

Hoyano and Graham<sup>14</sup> have photolyzed  $(\eta^5\text{-C}_5\text{Me}_5)\text{Os}(\text{CO})_2\text{H}$  in hexane or cyclohexane solutions under an  $\text{H}_2$  purge and have observed the formation of three species,  $(\eta^5\text{-C}_5\text{Me}_5)\text{Os}(\text{CO})\text{H}_3$ ,  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Os}_2(\text{CO})_2(\mu\text{-H})_2$ , and  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Os}_2(\text{CO})(\mu\text{-H})_2$ . In each case the CO-loss intermediate,  $(\eta^5\text{-C}_5\text{Me}_5)\text{Os}(\text{CO})\text{H}$ , was assumed to be involved.

The analogous ruthenium species,  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(\text{CO})_2(\mu\text{-H})_2$ , has been reported by Mahmoud, Rest, and Alt<sup>15</sup> upon photolysis of  $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2\text{Et}$  in pentane solutions. Upon loss of CO,  $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})\text{Et}$  undergoes  $\beta$  elimination to yield  $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})(\text{C}_2\text{H}_4)\text{H}$ , which, in turn, reacts with free CO to give **VI**. Continued photolysis of these solutions gives rise to  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(\text{CO})_2(\mu\text{-H})_2$ . In an effort to gain additional insight into the intermediates involved in the formation of these bridging hydride species, we examined the photolysis of both **V** and **VI** in frozen Nujol glasses.

## Results and Discussion

**Photolysis of  $(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)_2\text{Ru}_2(\text{CO})_4$ .** Nujol matrix photochemical studies were carried out using a liquid nitrogen cooled cryostat designed by Dr. Antony Rest of the University of Southampton. Typical sample preparation and experimental procedures have been reported previously.<sup>16</sup> Photolyses were conducted using a 350 W high-pressure mercury lamp with the irradiation wavelength ranges controlled using band-pass or cutoff optical filters.

$(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(\text{CO})_4$  was found to have very poor solubility in Nujol; thus the more soluble methyl derivative, **IV**, was used in the current studies. Room-temperature solutions of **IV** in Nujol were found to have bands attributable to the *trans*-bridged, 1959 and 1786  $\text{cm}^{-1}$ , and *trans*-nonbridged, 1967 and 1938  $\text{cm}^{-1}$ , isomers and a band at 2004  $\text{cm}^{-1}$  that is assigned to the symmetric stretch of the *cis*-bridged isomer, *vide infra*. The room-temperature spectrum of **IV** is presented in Figure 1a. Spectral data for all species are summarized in Table 1. Lowering the temperature of the Nujol solution to ca. 90 K resulted in the complete

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**Table 1. IR Spectral Positions of Carbonyl Bands of III, IV, V, and VI and Their Photoproducts in cm<sup>-1a</sup>**

compound	Nujol (90 K)	hexane	benzene	CHCl <sub>3</sub>
Cp <sub>2</sub> Os <sub>2</sub> (CO) <sub>4</sub> , <b>III</b>	2013 (w)	2010 (w)	2005 (w)	2005 (w)
	1968	1967	1960	1961
	1928	1931	1922	1921
CpOs(CO) <sub>2</sub> Cl				2043
				1983
Cp(CO) <sub>2</sub> Os– (C <sub>5</sub> H <sub>4</sub> )Os(CO) <sub>2</sub> H <sup>b</sup>			2027 (sh)	
			2012	
			2046	
Cp <sub>2</sub> Os <sub>2</sub> ( $\mu$ -CO) <sub>3</sub> ( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> CH <sub>3</sub> ) <sub>2</sub> Ru <sub>2</sub> – (CO) <sub>4</sub> , <b>IV</b>	1802			
<i>trans</i> -nonbridged, room temp	1966			
	1938			
<i>trans</i> -bridged, ca. 90 K	1957			
	1781			
<i>cis</i> -bridged, ca. 90 K	2004			
	1963			
(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Os <sub>2</sub> (CO) <sub>4</sub>	1780			
	1823			
CpOs(CO) <sub>2</sub> H, <b>V</b>	2090 (Os–H)	2090 <sup>c</sup>	2082	
	2017	2022 <sup>c</sup>	2010	
	1955	1961 <sup>c</sup>	1946	
CpOs(CO)H (C <sub>5</sub> H <sub>6</sub> )Os(CO) <sub>2</sub> <sup>b</sup>	1975			
	1998			
CpRu(CO) <sub>2</sub> H, <b>VI</b>	1931			
	2054 (Ru–H)	not obs		
	2029	2033 <sup>c</sup>		
CpRu(CO)H (C <sub>5</sub> H <sub>6</sub> )Ru(CO) <sub>2</sub> <sup>b</sup>	1969	1974 <sup>c</sup>		
	1953			
	2008			
	1942			

<sup>a</sup> Spectra are at room temperature unless otherwise noted. Cp =  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>. <sup>b</sup> Tentative assignment. <sup>c</sup> Petroleum ether.

disappearance of the bands of the *trans*-nonbridged isomer, Figure 1b. The bridging carbonyl band of the *trans*-bridging isomer shifted slightly to 1782 cm<sup>-1</sup> at the lower temperature. A difference spectrum suggests that the *trans*-nonbridged isomer converts to the *trans*-bridged isomer with little or no change in the quantity of the *cis*-bridged isomer. The observed shift of the nonbridged/bridged equilibrium toward the bridged species at low temperature is consistent with observations in the early literature.<sup>17</sup>

Photolysis of the frozen Nujol sample at  $\lambda_{\text{irr}} > 350$  nm was found by IR to have no significant effect on the appearance of the spectrum. Upon photolysis at  $\lambda_{\text{irr}} > 250$  nm, bands at 2131, 2004, 1965, 1931, and 1823 cm<sup>-1</sup> were formed, while bands of the *trans*-bridged isomer were depleted, Figure 2. Photolysis of this sample with  $\lambda_{\text{irr}} > 400$  nm resulted in depletion of the band at 2004 cm<sup>-1</sup> and reappearance of bands of the *trans*-bridged isomer. A band at  $2132 \pm 2$  cm<sup>-1</sup> is known to be associated with free CO in this matrix.

Prior to photolysis the intensities of the bridging and terminal bands of the *trans*-bridged isomer were almost equal, yet the intensity of the bridging carbonyl band in the difference spectrum, Figure 2, is much less than

that of the terminal carbonyl band. By carrying out a spectral subtraction to exactly null the bands of the *trans*-bridged isomer, new bands at 1963 and 1780 cm<sup>-1</sup> were revealed. The pattern of the bands, 2004 (s), 1963 (w), and 1780 (s) cm<sup>-1</sup>, is consistent with their being assigned to the *cis*-bridged isomer. A second band in the bridging region attributable to a symmetric stretching mode might also be expected, although it may be too weak to be observed, may overlap with the asymmetric stretching band, or may be obscured by the spectral manipulations.

The band observed at 1823 cm<sup>-1</sup> is very consistent with bands observed for the triply bridged species, ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Ru<sub>2</sub>( $\mu$ -CO)<sub>3</sub>, in frozen inert gases and is assigned to ( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>CH<sub>3</sub>)<sub>2</sub>Ru<sub>2</sub>( $\mu$ -CO)<sub>3</sub>. The small band at 1931 cm<sup>-1</sup> in the difference spectrum has not been assigned, while the 1965 cm<sup>-1</sup> band was found to be a subtraction artifact that merges into the 1963 cm<sup>-1</sup> band. It should be noted that continued photolysis of ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Ru<sub>2</sub>(CO)<sub>4</sub> in frozen inert gases resulted in a number of small bands that could not be assigned.<sup>4c</sup>

Unlike the *trans*-bridged isomer of ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Ru<sub>2</sub>(CO)<sub>4</sub> that is observed to undergo conversion to its nonbridged isomer upon photolysis, there is no evidence in these frozen Nujol solutions for the formation of the nonbridged isomer upon photolysis. In light of the dramatic thermal shift of the nonbridged/bridged equilibrium toward the bridged isomers, it is possible that photochemical bridge opening does occur but that this isomer is simply strongly disfavored at 90 K.

The photochemically reversible *trans*-bridged to *cis*-bridged interconversion may occur via a nonbridged intermediate by simple rotation or via a bridge-opening/radical formation process. We have no data to allow us to choose between these possible mechanisms. The photochemical transformations for **IV** are summarized in Scheme 1.

**Photolysis of ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Os<sub>2</sub>(CO)<sub>4</sub>, **III**** is known to exist in solution exclusively in a nonbridging conformation.<sup>18</sup> Carbonyl stretching bands of **III** in a number of solvents are reported in Table 1.

Brief photolysis of **III** in CHCl<sub>3</sub> in a borosilicate flask ( $\lambda > 300$  nm) results in complete disappearance of IR bands of **III** and appearance of bands at 2043 and 1983 cm<sup>-1</sup> identical to those reported for ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Os(CO)<sub>2</sub>Cl.<sup>19</sup> This result is analogous to the photolyses of **I**<sup>20</sup> and **II**<sup>21</sup> under similar conditions and provides strong evidence for Os–Os bond homolysis with formation of ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Os(CO)<sub>2</sub> radicals, Scheme 2a.

Photolysis of **III** in benzene was monitored by both IR and NMR. Brief photolysis results in the reduction in carbonyl bands of **III** and growth of new bands at

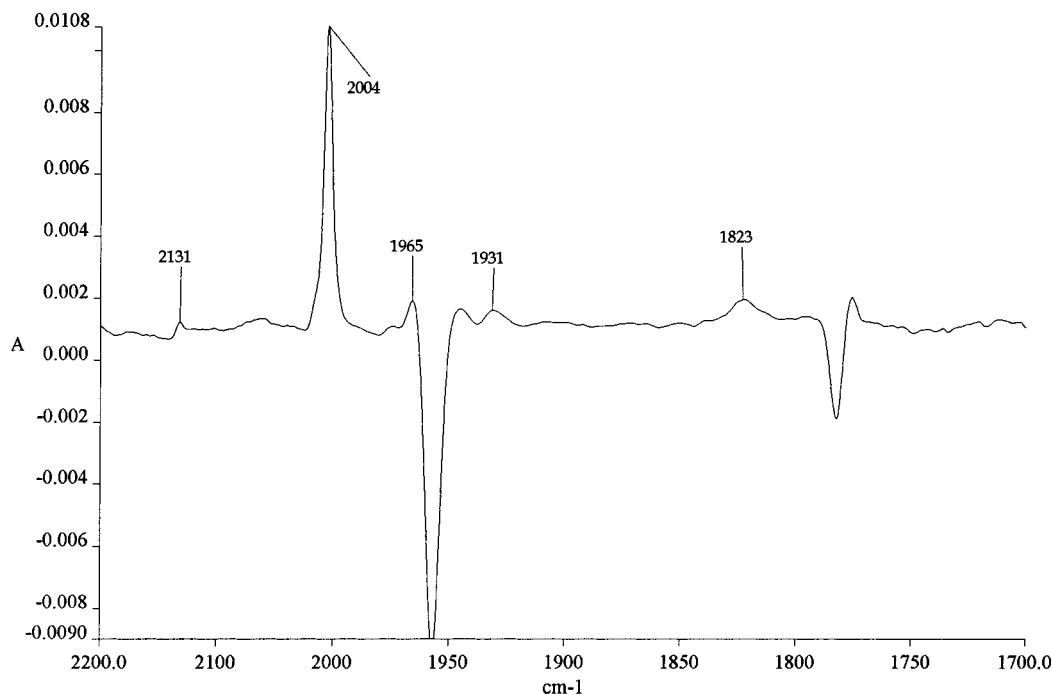
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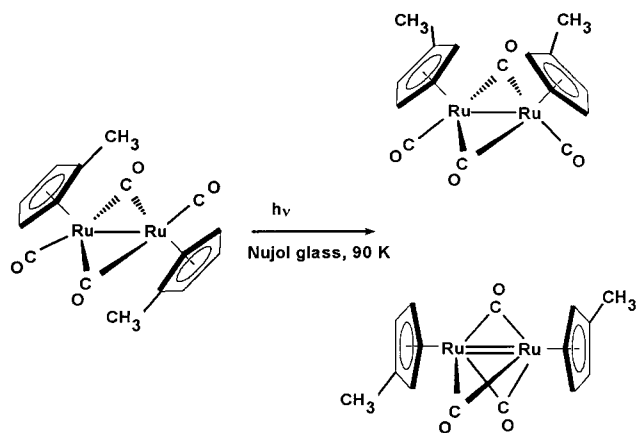
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**Figure 2.** Photolysis of  $(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)_2\text{Ru}_2(\text{CO})_4$  in Nujol at 90 K. Difference spectrum of  $(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)_2\text{Ru}_2(\text{CO})_4$  after 20 min photolysis without filter ( $\lambda_{\text{irr}} > 250$  nm) minus 20 min photolysis ( $\lambda_{\text{irr}} > 350$  nm).

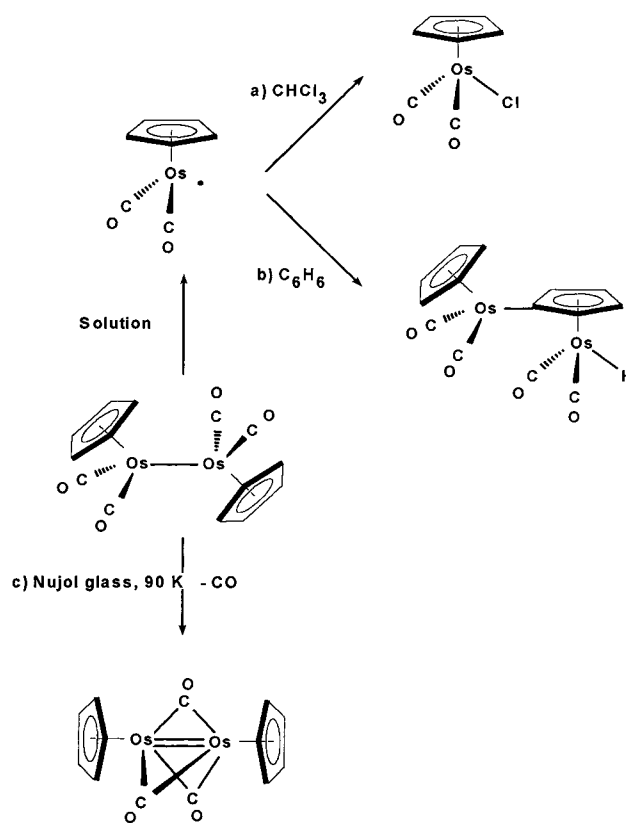
**Scheme 1. Photolysis Products of  $(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)_2\text{Ru}_2(\text{CO})_4$  in Nujol Glass, 90 K**



2027 (sh), 2012 (m), and 2046 (s).  $^1\text{H}$  NMR of a sample of **III** in  $\text{C}_6\text{D}_6$  was very clean with a single cyclopentadienyl resonance at 4.91 ppm.  $^{13}\text{C}$  NMR resonances were observed at 186.9 ppm (Os–CO) and 83.2 ppm ( $\text{C}_5\text{H}_5$ ). A 1 min photolysis ( $300 \text{ nm} < \lambda_{\text{max}} < 400 \text{ nm}$ ) results in the appearance of small new resonances at 4.62, 4.55, and  $-14.05$  ppm. After a total of 5 min of photolysis resonances at 4.72 (4), 4.62 (2), 4.55 (5), 4.41 (2), and  $-14.05$  (1) are observed (relative areas are approximate). Additional small resonances are observed in the ring resonance region, and a second small metal hydride resonance is observed at  $-13.68$  ppm. One additional resonance could be observed at 82.5 ppm in the  $^{13}\text{C}$  NMR spectrum. Overall photolysis conversion was estimated to be about 3%. For comparison,  $(\eta^5\text{-C}_5\text{H}_5)\text{-Os}(\text{CO})_2\text{H}$ , **V**, has resonances at 5.53 ppm (Cp) and  $-14.00$  ppm (Os–H) in  $\text{C}_6\text{D}_6$ .

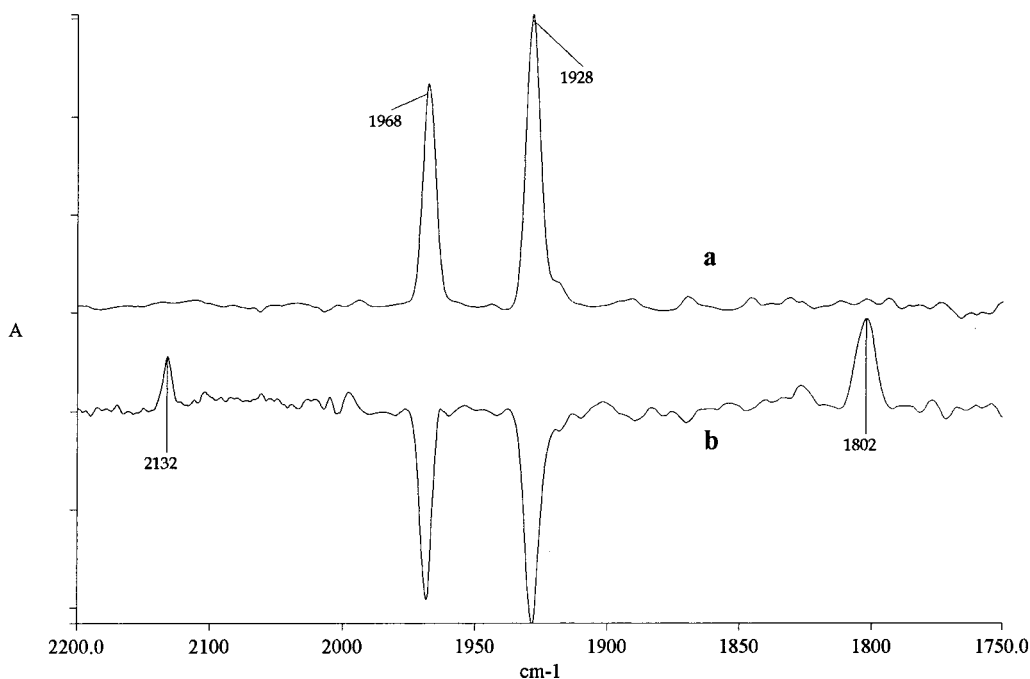
The IR and NMR evidence points to the formation of metal hydrides upon photolysis of **III** in benzene. Since we observe Os–H resonances in about the correct ratio for the new ring resonances, we believe that we can

**Scheme 2. Photolysis Products of  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Os}_2(\text{CO})_4$  in Solution and Nujol Glass**



preclude significant abstraction of deuterium from the  $\text{C}_6\text{D}_6$  solvent. **V** has IR bands at 2010 and  $1946 \text{ cm}^{-1}$  in benzene; thus the observed photoproduct band at  $2012 \text{ cm}^{-1}$  may be assigned to a  $\text{CpOs}(\text{CO})_2\text{H}$  fragment. The multiple ring resonances and the high-energy shoulder at  $2027 \text{ cm}^{-1}$  are completely analogous to features observed in the photolysis of **II** under identical condi-





**Figure 3.** Photolysis of  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Os}_2(\text{CO})_4$  in Nujol at ca. 90 K. (a) Sample prior to photolysis. (b) Difference spectrum of 20 min photolysis without filter ( $\lambda_{\text{irr}} > 250$  nm) minus 20 min photolysis ( $\lambda_{\text{irr}} > 350$  nm).

tions.<sup>22</sup> In the case of **II** evidence points to the formation of stairstep bimetallic complexes arising from the reaction of a metal-centered radical with the ring of a second radical or with the ring of an intact molecule of **II**. In the case of the osmium photolysis, the IR band at 2027  $\text{cm}^{-1}$  would be associated with the  $\text{Cp-Os}(\text{CO})_2\text{Cp}$  portion of the bimetallic species. The likely product in this process is illustrated in Scheme 2b. Unfortunately the appearance of secondary photolysis products early in the photolysis precludes isolation and full characterization of the photoproducts.

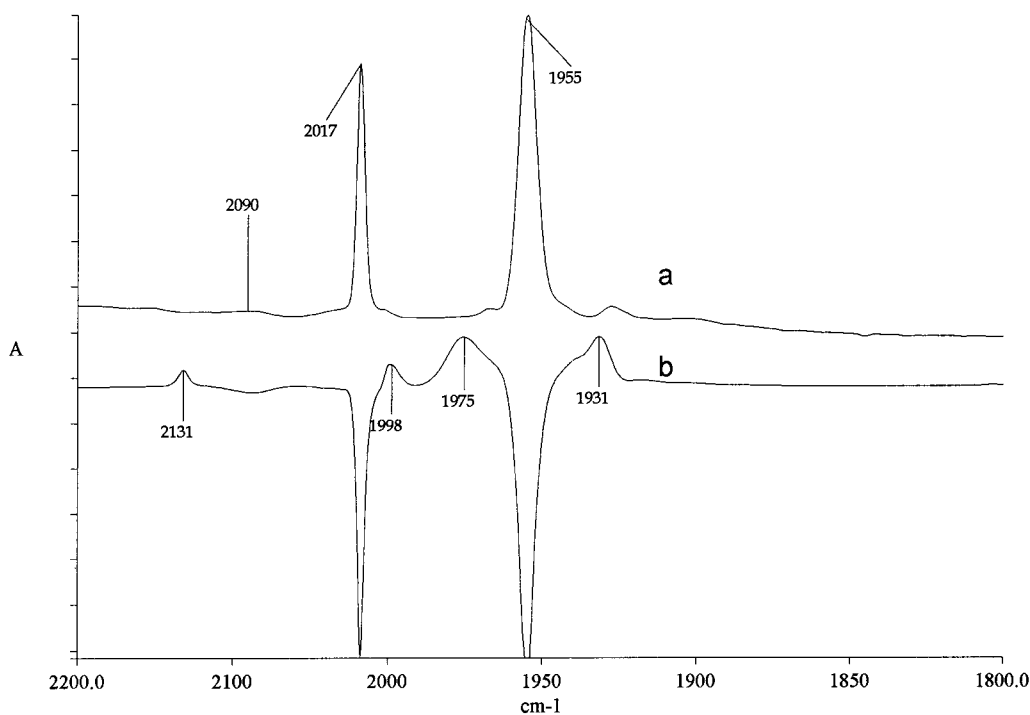
**III** is weakly soluble in Nujol; however dilute solutions free of particulate were obtained through centrifugation of thoroughly ground mulls. Particles in the Nujol solutions result in broadened IR bands and generally degrade the quality of the resultant spectra. Nujol glass solutions (ca. 90 K) of **III** were found to have IR bands at 2013 (w), 1968 (s), and 1928 (s)  $\text{cm}^{-1}$ , Figure 3a. Photolysis with wavelengths longer than 330 nm was found to have no measurable effect on the spectrum of the sample. Photolysis ( $250 \text{ nm} < \lambda_{\text{max}} < 330 \text{ nm}$ ) resulted in bleaching of the bands of **III** and growth of new bands at 2132 and 1802  $\text{cm}^{-1}$ , Figure 3b. While the signal-to-noise ratio of this spectrum is certainly acceptable, its somewhat poor quality is attributable to the relatively small conversion of **III** into its CO-loss products. This low conversion may result from a high probability of radical formation and recombination that competes with CO loss, or from back-photolysis from long wavelength light in the photolysis beam. Repeated attempts to improve on the quality of these spectra were unsuccessful, indicating that the spectral quality is inherent in the photolysis, not in the sample preparation. The band at  $2132 \pm 2 \text{ cm}^{-1}$  is known to be associated with "free" CO in Nujol matrixes, while the band at 1802  $\text{cm}^{-1}$  is consistent with a triply carbonyl-

bridged species,  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Os}_2(\mu\text{-CO})_3$ , Scheme 2c. The corresponding iron and ruthenium triply carbonyl-bridged species have IR bands at 1813 and 1829  $\text{cm}^{-1}$ , respectively in frozen methane matrixes at 12 K.<sup>4</sup> The same iron species has been observed in poly(vinyl chloride) at 77 K<sup>4a</sup> and in time-resolved spectra of room-temperature solutions.<sup>1</sup> There was no evidence for bands that might be attributed to  $(\eta^5\text{-C}_5\text{H}_5)\text{Os}(\text{CO})_2$  radicals. It is presumed that radicals formed upon photolysis are trapped within the solvent cage and readily recombine. Bands observed in the photolyses of **I** and **II** in frozen methane matrixes (12 K) have been associated with the  $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2$  radicals.<sup>4c</sup>

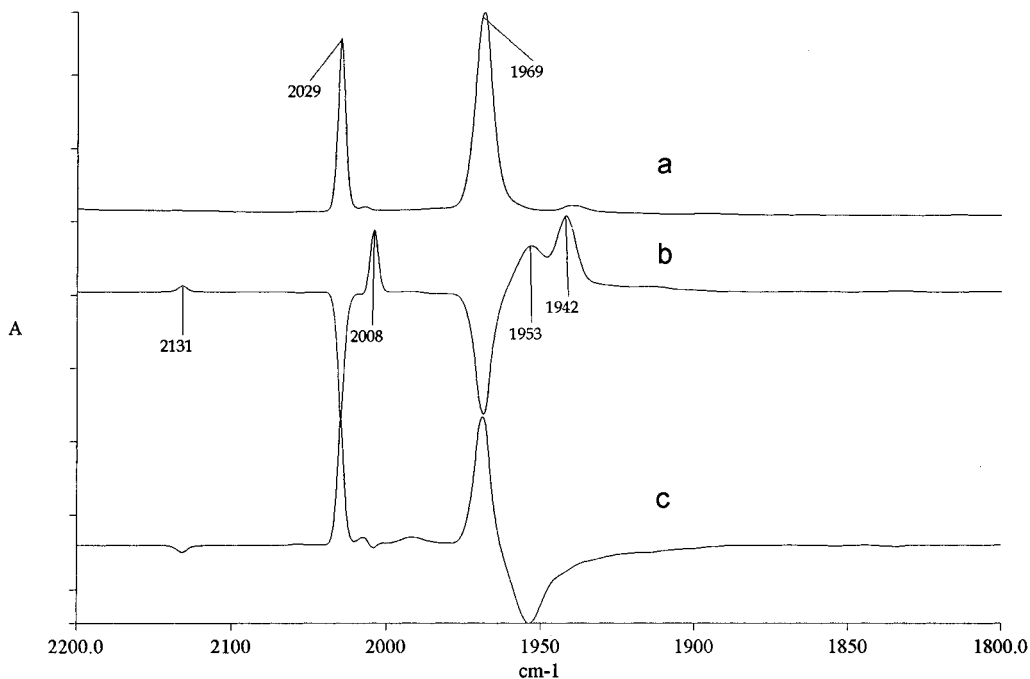
**Photolysis of  $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2\text{H}$ , Where M = Os and Ru.** In frozen Nujol **V** is found to have strong carbonyl bands at 2017 and 1955  $\text{cm}^{-1}$  and a weak band at 2090  $\text{cm}^{-1}$  that has been assigned to the Os-H stretch, Figure 4a. Photolysis with  $\lambda > 400$  nm was found to have no effect on the spectrum. Photolysis ( $260 \text{ nm} < \lambda_{\text{max}} < 400 \text{ nm}$ ) results in decrease of the bands of **IV** and growth of new bands at 2131, 1998, 1975, and 1931  $\text{cm}^{-1}$ , Figure 4b. Back photolysis at  $\lambda > 400$  nm resulted in no change in the product spectrum. Attempts at annealing the sample by carrying out controlled warming cycles resulted in complex changes that could not be interpreted.

In frozen Nujol **VI** is found to have carbonyl bands at 2029 and 1969  $\text{cm}^{-1}$  and a very weak Ru-H band at 2054  $\text{cm}^{-1}$  (not visible in the Figure), Figure 5a. Photolysis of **VI**,  $\lambda > 340$  nm, resulted in no significant spectral changes; however, higher energy photolysis,  $260 \text{ nm} < \lambda_{\text{max}} < 400 \text{ nm}$ , resulted in a decrease in the intensity of the bands of **VI** and growth of new bands at 2131, 2008, 1953, and 1942  $\text{cm}^{-1}$ , Figure 5b. Back photolysis at  $\lambda > 400$  nm resulted in the bands at 2131 and 1953  $\text{cm}^{-1}$  decreasing, while bands of the **VI** grew in, Figure 5c. A small, unassigned band at 1991  $\text{cm}^{-1}$  was also observed to grow in under these conditions.

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**Figure 4.** Photolysis of  $(\eta^5\text{-C}_5\text{H}_5)\text{Os}(\text{CO})_2\text{H}$  in Nujol at ca. 90 K. (a) Sample prior to photolysis. (b) Difference spectrum of 20 min photolysis ( $260 \text{ nm} < \lambda_{\text{max}} < 400 \text{ nm}$ ) minus 20 min photolysis ( $\lambda_{\text{irr}} > 400 \text{ nm}$ ).

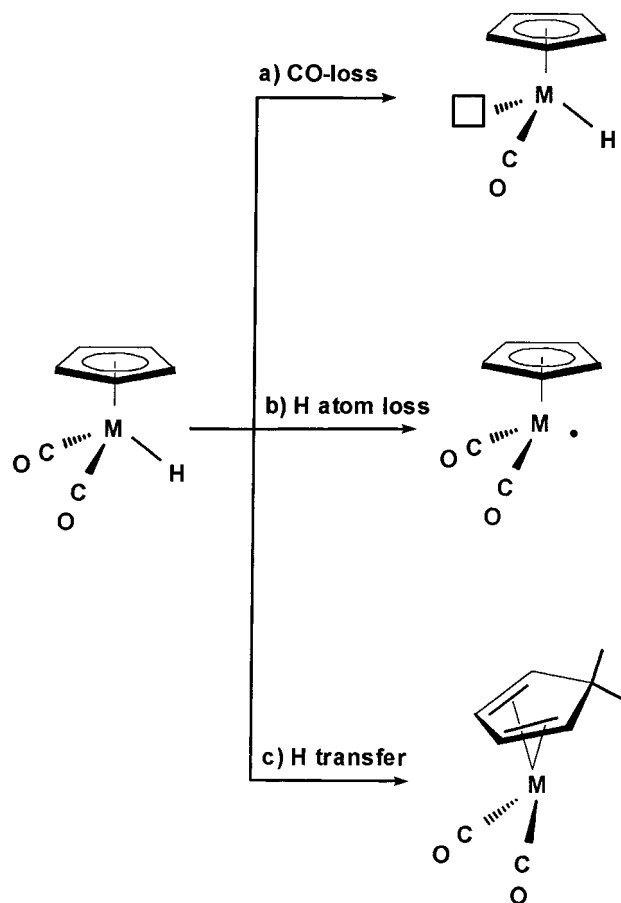


**Figure 5.** Photolysis of  $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2\text{H}$  in Nujol at ca. 90 K. (a) Sample prior to photolysis. (b) Difference spectrum of 20 min photolysis ( $260 \text{ nm} < \lambda_{\text{max}} < 400 \text{ nm}$ ) minus 20 min photolysis ( $\lambda_{\text{irr}} > 400 \text{ nm}$ ). (c) Difference spectrum of 20 min back photolysis ( $\lambda > 400 \text{ nm}$ ) minus 20 min photolysis ( $260 \text{ nm} < \lambda_{\text{max}} < 400 \text{ nm}$ ).

As expected, the high-energy photolyses of **V** and **VI** result in CO loss ( $\nu \text{ CO} = 2132 \text{ cm}^{-1}$ ); however the appearance of three bands in the terminal carbonyl region was surprising. The presumed CO-loss species,  $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})\text{H}$  or  $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})(\text{S})\text{H}$ , where S is solvent, must have only one carbonyl stretching band. For **VI**, back photolysis allows us to unequivocally assign the band at  $1953 \text{ cm}^{-1}$  to  $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})\text{H}$ . This assignment is also consistent with the photolysis of  $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2\text{CH}_3$ . IR bands of  $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2\text{-CH}_3$  are reported to be  $2020$  and  $1960 \text{ cm}^{-1}$  in a

methane matrix, and the photolysis product,  $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})\text{CH}_3$ , was found to have a band at  $1943 \text{ cm}^{-1}$ .<sup>15</sup> We assign the band at  $1975 \text{ cm}^{-1}$  to  $(\eta^5\text{-C}_5\text{H}_5)\text{-Os}(\text{CO})\text{H}$ , although we note that the much higher frequency of this band relative to its ruthenium analogue may suggest a stronger interaction between the osmium species and the Nujol solvent than is the case with ruthenium. The CO-loss mechanism is presented in Scheme 3a.

Bands at  $1997$  and  $1928 \text{ cm}^{-1}$  have been assigned to the  $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2$  radical in methane matrices (12

**Scheme 3. Possible Photochemical Pathways for  $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2\text{H}$ , Where M = Ru and Os**

K);<sup>4c</sup> however recent time-resolved studies of **II** in *n*-heptane clearly reveal bands of the radical at 2011 and 1949  $\text{cm}^{-1}$ .<sup>6</sup> The similarity of the radical bands in heptane solution to those of the second photoproduct in Nujol raises the possibility that  $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2$ , and by inference  $(\eta^5\text{-C}_5\text{H}_5)\text{Os}(\text{CO})_2$ , radicals may arise by homolysis of the M–H bond with elimination of a hydrogen atom, Scheme 3b. Such a reaction has been observed in the photolysis of  $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{H}$ , M = Mo or W, in a solid CO matrix.<sup>23</sup> Under these conditions, photolysis results in formation of the corresponding  $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3$  radical along with the stable HCO radical. This reaction was not observed in methane or argon matrixes.

An alternative formulation for the photoproducts of **V** and **VI** is the structural isomer,  $(\eta^4\text{-C}_5\text{H}_6)\text{M}(\text{CO})_2$ , that might arise from transfer of the metal hydride to the cyclopentadienyl ring, Scheme 3c. For ruthenium this is, of course, the intermediate believed to form upon CO loss from  $(\eta^4\text{-C}_5\text{H}_6)\text{Ru}(\text{CO})_3$  during the synthesis of  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(\text{CO})_4$  from  $\text{Ru}_3(\text{CO})_{12}$  and cyclopentadiene. Humphries and Knox<sup>24</sup> have reported the low-yield synthesis of  $(\eta^4\text{-C}_5\text{H}_6)\text{Ru}(\text{CO})_3$ , **VII**, as a pale yellow oil contaminated with excess cyclopentadiene. We have reproduced this synthesis and have examined the photolysis of **VII** in a Nujol matrix. **VII** is found to have IR

bands at 2059, 1994, and 1982  $\text{cm}^{-1}$ . No spectral changes were observed with photolysis wavelengths longer than 400 nm. Upon photolysis ( $340 \text{ nm} < \lambda_{\text{max}} < 400 \text{ nm}$ ) bands for free CO, **VI** and bands at 2008 and 1942  $\text{cm}^{-1}$  were observed. **VI** is the dominant product in this photolysis. Minor bands were also observed that may be the result of reactions between photofragments and cyclopentadiene in the matrix. Unfortunately the strong and concurrent formation of **VI** makes it impossible to establish whether the species with bands at 2008 and 1942  $\text{cm}^{-1}$  arises directly from **VII** or indirectly from **VI**.

Rest and co-workers<sup>25</sup> have examined the photolysis of a number of iron( $\eta^4$ -polyene)carbonyl compounds in frozen gas matrixes at 12 K. In methane  $(\eta^4\text{-C}_5\text{H}_6)\text{Fe}(\text{CO})_3$  was reported to have carbonyl stretching bands at 2048, 1980, and 1970  $\text{cm}^{-1}$ , and its photolysis product,  $(\eta^4\text{-C}_5\text{H}_6)\text{Fe}(\text{CO})_2$ , has bands at 1991 and 1926  $\text{cm}^{-1}$ . For comparison,  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{H}$  has bands at 2020 and 1963  $\text{cm}^{-1}$  in methane.

Finally, Wrighton and co-workers<sup>26</sup> have examined the photochemistry of  $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$  in methylcyclohexane at ca. 90 K. In this medium  $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$  has IR bands at 2061, 2004, and 1993  $\text{cm}^{-1}$ . Upon UV photolysis, this compound lost CO to form  $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_2$ , which was reported to have carbonyl stretching bands at 2020 and 1948  $\text{cm}^{-1}$ . By comparison with these ruthenium and iron analogues,  $(\eta^4\text{-C}_5\text{H}_6)\text{Ru}(\text{CO})_2$  would be expected to have IR bands in the range 2020–2000 and 1940–1950  $\text{cm}^{-1}$ .

The present data do not allow us to firmly establish the identity of the second species formed upon photolysis of **V** and **VI**, although, in the absence of any obvious hydrogen atom acceptors, we lean toward  $(\eta^4\text{-C}_5\text{H}_6)\text{M}(\text{CO})_2$  as the more likely assignment. Whether this species might arise from direct metal hydride to ring transfer or via a radical mechanism cannot be determined at this time.

### Experimental Section

**III**,<sup>10</sup> **IV**,<sup>17a</sup> **V**,<sup>10</sup> **VI**,<sup>11</sup> and **VII**<sup>23</sup> were prepared by literature procedures. **VI** is very air sensitive; thus Nujol samples were prepared under  $\text{N}_2$  using Nujol that had been degassed under vacuum with heating. IR spectra were recorded on a Perkin-Elmer Spectrum 1000 FTIR spectrometer at 4  $\text{cm}^{-1}$  resolution. NMR spectra were recorded on a Bruker 500 MHz NMR spectrometer and were referenced against standard solvent resonances.

Nujol photolysis studies were carried out using a liquid nitrogen cryostat and techniques as previously described.<sup>21</sup>

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