Photochemistry of (.eta.3-C3H5)Ru(CO)3Br: spectroscopic evidence for the intermediates (.eta.3-C3H5)Ru(CO)2Br and [(.eta.3-C3H5)Ru(CO)2(.mu.-Br)]2

Yee Min. Wuu, and Mark S. Wrighton

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Photochemistry of $(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$: Spectroscopic Evidence for the Intermediates $(\eta^3\text{-}C_3H_5)Ru(CO)_2Br$ and $[(\eta^3\text{-}C_3H_5)Ru(CO)_2(\mu\text{-}Br)]_2$

Yee-Min Wuu and Mark S. Wrighton*

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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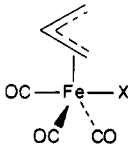
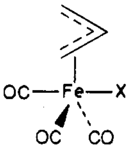
The complex $(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$ exists in solution in a conformational equilibrium between endo and exo isomers differing principally in the orientation of the allyl group. At room temperature, the two isomers interconvert slowly ($t_{1/2} > 10$ min) and the endo isomer predominates (>95%). Near-UV photolysis of $(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$ in alkane solution shifts the equilibrium toward *exo*-$(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$. Thermal equilibrium is reestablished in the dark at 298 K. An intermediate in the 298 K photochemical rearrangement is shown by IR, ^1H NMR, and mass spectrometry studies to be $[(\eta^3\text{-}C_3H_5)Ru(CO)_2(\mu\text{-}Br)]_2$. Consistent with the intermediacy of dihalo-bridged species, irradiation of a mixture of $(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$ and $(\eta^3$-2-methylallyl$)Ru(CO)_3Cl$ yields "crossover" products $(\eta^3\text{-}C_3H_5)Ru(CO)_3Cl$ and $(\eta^3$-2-methylallyl$)Ru(CO)_3Br$. Near-UV irradiation of $(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$ at 77 K in a 2-methyltetrahydrofuran matrix results in loss of CO as evidenced by the growth of an IR absorption due to free CO. At room temperature, the 16e $(\eta^3\text{-}C_3H_5)Ru(CO)_2Br$ dimerizes forming the dibromo-bridged dimer $[(\eta^3\text{-}C_3H_5)Ru(CO)_2(\mu\text{-}Br)]_2$. The dimer subsequently reacts with photoreleased CO to generate >90% *exo*-$(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$ with <10% of the endo isomer being detected. The formation rate of the exo isomer is much faster than the rate for thermal isomerization of *exo*-$(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$ to *endo*-$(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$. Change in the ratio of *endo*- and *exo*-$(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$ upon near-UV irradiation clearly indicates that $[(\eta^3\text{-}C_3H_5)Ru(CO)_2(\mu\text{-}Br)]_2$ and CO yield *exo*-$(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$ more rapidly than *endo*-$(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$. Irradiation of $(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$ in 3-methylpentane at 298 K in the presence of excess 2e donor ligands (L = PPh_3, C_2H_4, ^{13}CO) results in the direct trapping of $(\eta^3\text{-}C_3H_5)Ru(CO)_2Br$ to form $(\eta^3\text{-}C_3H_5)Ru(CO)_2(L)Br$ with only negligible yields of $[(\eta^3\text{-}C_3H_5)Ru(CO)_2(\mu\text{-}Br)]_2$. Interestingly, C_2H_4 does not react with $[(\eta^3\text{-}C_3H_5)Ru(CO)_2(\mu\text{-}Br)]_2$ to form $(\eta^3\text{-}C_3H_5)Ru(CO)_2(C_2H_4)Br$ under conditions where photolysis of $(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$ does yield $(\eta^3\text{-}C_3H_5)Ru(CO)_2(C_2H_4)Br$. This result suggests that reaction of $[(\eta^3\text{-}C_3H_5)Ru(CO)_2(\mu\text{-}Br)]_2$ with L = CO or PPh_3 to yield $(\eta^3\text{-}C_3H_5)Ru(CO)_2(L)Br$ is initiated by attack on the dimer, not capture of $(\eta^3\text{-}C_3H_5)Ru(CO)_2Br$ from the dimer.

In this paper we wish to report the photochemistry of $(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$. The primary photoprocess is CO loss to yield $(\eta^3\text{-}C_3H_5)Ru(CO)_2Br$ which can be scavenged by 2e donor ligands or oxidative addition substrates. In the absence of reactive molecules the 16e intermediate dimerizes to give $[(\eta^3\text{-}C_3H_5)Ru(CO)_2(\mu\text{-}Br)]_2$ which back-reacts with CO to give only *exo*-$(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$ which thermally isomerizes to an endo-rich (>95%) distribution of *endo*- and *exo*-$(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$. This investigation was stimulated by our observation that irradiation of $(\eta^3\text{-}C_3H_5)Fe(CO)_3H$, which is inert only below 195 K, yields a new compound without net CO loss.[1] The new compound, which reverts thermally to $(\eta^3\text{-}C_3H_5)Fe(CO)_3H$, is assigned to the conformational isomer of $(\eta^3\text{-}C_3H_5)Fe(CO)_3H$ having the allyl group rotated by 180°.

π-Allyl complexes of certain transition metals are well-known to exist as two isomers.[2-5] In particular, two isomers are observed for each of the complexes $(\eta^3\text{-}C_3H_5)Fe(CO)_3X$ (X = Cl, Br, I, NCO).[5] The geometry of both isomers is approximately octahedral with the π-allyl ligand occupying two cis positions. In the endo isomer, the central hydrogen of the allyl moiety points away from the halide. In the exo isomer, the central hydrogen points toward the halide. The two geometric isomers of these iron complexes do not interconvert at room temperature. Faller determined that in solution the predominant isomer is the endo isomer.[5b] The crystal structures of $(\eta^3\text{-}C_3H_5)Fe(CO)_3X$ (X = Br,[6] I[7]) have been reported and show the complexes to have the endo structure.



endo



exo

We present here the results of an investigation of the photochemistry of $(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$. Irradiation of an equilibrium mixture of *endo*-$(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$ and *exo*-$(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$ at room temperature in solution results in enrichment of the mixture in *exo*-$(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$. Irradiation of $(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$ in a low-temperature matrix demonstrates that the primary photoprocess is loss of CO. Photolysis of $(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$ in the absence of reactive molecules yields a species which we have characterized by IR, ^1H NMR, and mass spectrometry and assigned to be $[(\eta^3\text{-}C_3H_5)Ru(CO)_2(\mu\text{-}Br)]_2$.

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* To whom correspondence should be addressed.

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Table I. Chemical Shifts (ppm from TMS) and Isomer Ratios of *endo*- and *exo*-(η^3-C_3H_5)M(CO)$_3$Br[a]

		endo			exo			
compd	solv	central	syn	anti	central	syn	anti	isomer ratio endo/exo
(η^3-C_3H_5)Ru(CO)$_3$Br	$CDCl_3$	5.14	4.08	3.13	5.47	3.84	2.59	40
	C_6D_6	4.05	3.20	2.95	5.23	3.14	1.69	36
								7.9[b]
	C_6D_{12}	5.00	3.94	3.17	5.51	3.66	2.45	28
(η^3-C_3H_5)Fe(CO)$_3$Br	$CDCl_3$	5.02	4.49	3.57	5.57	4.18	2.63	5.3

[a] All spectra record at 298 K. [b] After 1 min near-UV irradiation of the same solution and approximately 10-min acquisition time (Figure 2).

Table II. IR Data for Relevant Complexes

compd	medium (*T*, K)	band maxima, cm^{-1} (rel abs)
endo-(η^3-C_3H_5)Ru(CO)$_3$Br	3-MP (298)	2109 (1.0), 2060 (1.4), 2016 (1.3)
	2-MeTHF (298)	2107 (1.2), 2052 (1.3), 2020 (1.0)
	2-MeTHF (90)	2106 (1.5), 2046 (1.4), 2025 (1.0)
exo-(η^3-C_3H_5)Ru(CO)$_3$Br	3-MP (298)	2107 (1.0), 2055 (1.1), 2021 (1.2)
[(η^3-C_3H_5)Ru(CO)$_2$Br]$_2$	3-MP (298)	2047 (1.0), 1985 (1.6)
(η^3-C_3H_5)Ru(CO)$_2$(2MeTHF)Br	2-MeTHF (90)	2036 (1.0), 1967 (1.5)
(η^3-C_3H_5)Ru(CO)$_2$(PPh$_3$)Br	3-MP (298)	2044 (1.0), 1978 (1.5)
(η^3-C_3H_5)Ru(CO)$_2$(C_2H_4)Br	3-MP (298)	2072 (1.0), 1992 (1.3)
(η^3-C_3H_5)Ru(CO)$_2$(H)(SiEt$_3$)Br	3-MP (298)	2047 (1.5), 2008 (1.0)
(η^3-C_3H_5)Ru(CO)$_2$(^{13}CO)$_{cis}$Br	3-MP (298)	2097, 2034, 2008
		2096, 2033, 2009[a] 2094, 2032, 2010[b]
(η^3-C_3H_5)Ru(CO)$_2$(^{13}CO)$_{trans}$Br		*c*, *c*, 1975
		2106, 2060, 1974[a] 2103, 2055, 1980[b]
Ru(CO)$_4$(C_2H_4)	3-MP (298)	2104 (1.90), 2023 (17.4), 1996 (8.6)
Ru(CO)$_4$(η^2-C_3H_5Br)	3-MP (298)	2108 (1.0), 2053 (8.0), 2032 (2.0)
endo-(η^3-C_3H_5)Fe(CO)$_3$Br	3-MP (298)	2089 (1.1), 2045 (1.2), 2011 (190)
exo-(η^3-C_3H_5)Fe(CO)$_3$Br	3-MP (298)	2087 (1.0), 2041 (1.0), 2015 (1.3)
[(η^3-C_3H_5)Fe(CO)$_2$Br]$_2$	3-MP (298)	2033 (190), 1982 (1.3)

[a] Calculated from *endo*-(η^3-C_3H_5)Ru(CO)$_3$Br by using the force-field method. [b] Calculated from *exo*-(η^3-C_3H_5)Ru(CO)$_3$Br by using the force-field method. [c] Overlapping with all ^{12}CO complex.

[(η^3-C_3H_5)Ru(CO)$_2$(μ-Br)]$_2$ reacts with CO yielding *exo*-(η^3-C_3H_5)Ru(CO)$_3$Br which thermally reverts to *endo*-(η^3-C_3H_5)Ru(CO)$_3$Br.

Experimental Section

Instruments and Equipment. IR spectra were recorded with a Nicolet 7199 or 60SX Fourier transform spectrometer; ^{1}H NMR spectra were recorded on either a Bruker 250 or a 270-MHz Fourier transform spectrometer. Low-temperature IR spectra were recorded in deoxygenated 2-methyltetrahydrofuran (2-MeTHF) solution samples held in a Specac Model P/N 21.000 variable-temperature cell with CaF_2 windows, with liquid N_2 as coolant. Mass spectral measurements were performed on either a Finnigan MAT 731 or 8200 instrument.

Irradiations. A Bausch and Lomb SP208 high-pressure Hg lamp (output filtered with Pyrex and 10 cm of H_2O to remove deep UV and IR light) was used for low-temperature irradiations. A 550-W Hanovia medium-pressure lamp was used for preparative photolysis. A Model A high-energy micro pulser from Xenon Corp. was used for flash photolysis. The pulser is equipped with the Xenon FP series of micropulse flashtubes used at a discharge voltage of ~5 kV. Samples of 3 mM (η^3-C_3H_5)Ru(CO)$_3$Br (with 0.05 M PPh$_3$; 3.0 mL) for quantum yields at 313 nm were freeze–pump–thaw degassed in 13 × 100 mm Pyrex test tubes with constrictions and hermetically sealed. Irradiations for quantum yield determinations were carried out in a merry-go-round.[8] The light source was a 450-W medium-pressure Hg lamp (Hanovia) equipped with Corning glass filters and basic aqueous CrO_4^{2-} solution to isolate the 313-nm Hg emission. Ferrioxalate actinometry[9] was used to determine the excitation rate which was typically 10^{-8} ein/min.

Table III. ^{1}H NMR Data for Relevant Complexes[a]

compd	chem shift, δ vs Si(CH$_3$)$_4$
(η^3-C_3H_5)Ru(CO)$_3$Br	5.00 m (1 H), 3.94 d (2 H), 3.17 d (2 H)
(η^3-C_3H_5)Ru(CO)$_3$Cl	5.11 m (1 H), 4.00 d (2 H), 2.97 d (2 H)
(η^3-2-MeC$_3H_4$)Ru(CO)$_3$Br	2.04 s (3 H), 3.85 s (2 H), 3.17 s (2 H)
(η^3-2-MeC$_3H_4$)Ru(CO)$_3$Cl	2.02 s (3 H), 3.90 s (2 H), 2.96 s (2 H)
[(η^3-C_3H_5)Ru(CO)$_2$(Br)]$_2$	5.21 m (1 H), 4.60 d (2 H), 4.32 d (2 H)
(η^3-C_3H_5)Ru(CO)$_2$PPh$_3$Br[b]	7.60 m (6 H), 7.41 m (9 H), 5.04 m (1 H), 3.89 m (1 H), 3.73 m (1 H), 3.18 dd (1 H), 2.83 d (1 H)
(η^3-C_3H_5)Ru(CO)$_2$(C_2H_4)Br[c]	3.55–3.72 m (4 H), 3.48 m (1 H), 3.28–3.40 m (2 H), 3.14 m (2 H)

[a] All spectra are at 298 K in cyclohexane-d_{12} solvent, unless otherwise noted. [b] In chloroform-d_1 solvent. [c] In C_6D_6 solvent.

Chemicals. All solvents were reagent grade and freshly distilled before use. PPh$_3$ (Aldrich) was recrystallized three times from absolute EtOH. C_3H_5Br, C_3H_5Cl, and C_4H_7Cl were obtained from Aldrich and were passed through Al_2O_3 prior to use. Research grade CO and C_2H_4 were obtained from Matheson. ^{13}CO (99% ^{13}C) was obtained from Cambridge Isotope Laboratories. Ru$_3$(CO)$_{12}$ and Fe(CO)$_5$ were obtained from Strem Chemicals. The Ru$_3$(CO)$_{12}$ was used as received, and the Fe(CO)$_5$ was passed through Al_2O_3 prior to use. All reactions and manipulations of organometallic reagents were carried out by using standard Schlenk techniques under an Ar atmosphere or in a Vacuum Atmospheres drybox under N_2.

(η^3-C_3H_5)Ru(CO)$_3$Br, (η^3-C_3H_5)Ru(CO)$_3$Cl, and (η^3-2-methylallyl)Ru(CO)$_3$Cl were prepared according to the literature procedure.[10] Likewise, (η^3-C_3H_5)Fe(CO)$_3$Br was prepared according to literature procedure.[11] Spectroscopic (IR and ^{1}H NMR) data for these and other complexes are given in Tables I–III.

[(η^3-C_3H_5)Ru(CO)$_2$(μ-Br)]$_2$ was prepared by irradiation of a saturated isooctane solution of (η^3-C_3H_5)Ru(CO)$_3$Br with a 550-W Hanovia medium-pressure Hg lamp. The solution was placed in a 30 × 3 cm diameter Pyrex test tube and purged vigorously with a stream of Ar. The evaporated solvent was constantly replenished by cannula transfer of fresh, deoxygenated solvent into the test tube. The reaction was monitored by IR spectroscopy. In order

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to avoid secondary photodecomposition, the irradiation was discontinued after approximately 50% conversion to $[(\eta^3\text{-}C_3H_5)Ru(CO)_2(\mu\text{-}Br)]_2$ and the solvent was removed in vacuo. The yellow residue was established to be a mixture of $(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$ and $[(\eta^3\text{-}C_3H_5)Ru(CO)_2(\mu\text{-}Br)]_2$ by IR, ^1H NMR, and mass spectrometry.

$(\eta^3\text{-}C_3H_5)Ru(CO)_2(PPh_3)Br$ was prepared by irradiation with a 550-W Hanovia medium-pressure Hg lamp of an isooctane solution of $(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$ (0.2 g) and PPh_3 (0.4 g) under a purge of Ar to remove photogenerated CO. After 30 min a pale yellow powder precipitated that was filtered and dried (0.32 g). The product was further purified by recrystallization from CH_2Cl_2/hexane, and IR and ^1H NMR are consistent with this known[18b] compound.

$(\eta^3\text{-}C_3H_5)Ru(CO)_2(C_2H_4)Br$ was prepared by irradiation of 5 mM $(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$ in a continuously C_2H_4-purged alkane solution using a Hanovia 550-W medium-pressure Hg lamp. The irradiation was discontinued after 40% conversion to $(\eta^3\text{-}C_3H_5)Ru(CO)_2(C_2H_4)Br$ in order to avoid secondary photodecomposition. The yellow compound was established to be $(\eta^3\text{-}C_3H_5)Ru(CO)_2(C_2H_4)Br$ by IR and ^1H NMR. Attempted isolation results in loss of C_2H_4 (upon solvent removal) to yield $[(\eta^3\text{-}C_3H_5)Ru(CO)_2(\mu\text{-}Br)]_2$.

Results and Discussion

(a) ^1H NMR Spectroscopy of $(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$: Evidence for *Endo* and *Exo* Isomers. The preparation of $(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$ was reported previously and indicated that only one isomer was present.[10] However, we find that the ^1H NMR spectrum of $(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$ in several solvents has two sets of resonances (Table I) for the allyl ligand, the dominant set attributable to the endo isomer and the other set attributable to the exo isomer. Each set of observed resonances consists of a multiplet and two doublets[12] having a ratio of areas of 1:2:2. This spectrum, characteristic of an AM_2X_2 system, is consistent with the expected π-allyl structure for $(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$. In $CDCl_3$, the ratio of areas of the two sets of resonances is 40:1. The resonances for the syn and anti hydrogens of the allyl group[13] in the minor isomer are shifted upfield by 0.5–1 ppm compared to those for the major isomer. The difference in chemical shift is analogous to that which is observed for the endo and exo isomers of $(\eta^3\text{-}C_3H_5)Fe(CO)_3Br$ (Table I). Faller and Adams[5b] have measured ^1H NMR spectra for $(\eta^3\text{-}C_3H_5)Fe(CO)_3X$ (X = I, Br, Cl, NCO). They found that in each complex the resonances due to the syn and anti hydrogens of the exo isomer were at higher field than the corresponding resonances of the endo isomer. By analogy, the major isomer of $(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$ is assigned to *endo*-$(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$ and the minor isomer to *exo*-$(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$.

Polarity of the solvent has a small effect on the ratio of endo to exo isomers. The equilibrium constants (K = endo/exo) presented in Table I were obtained by integration of the proton resonances for *exo*- and *endo*-$(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$ in the ^1H NMR spectrum taken at 298 K. *endo*-$(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$ is calculated from the equilibrium constant to be ~2 kcal/mol more stable than the *exo*-$(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$ in $CDCl_3$ solution. The exo and endo isomers of the analogous Fe complexes differ by ~1 kcal/mol.

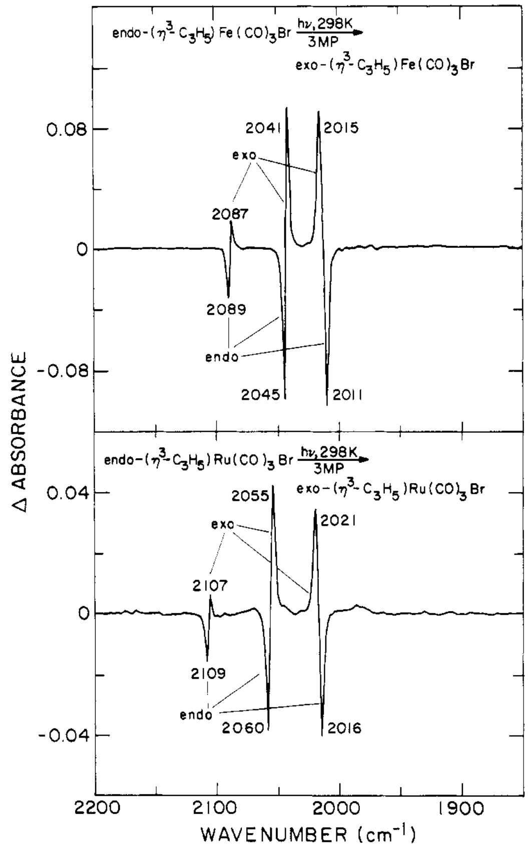

Figure 1. (a) IR difference spectral changes due to near-UV irradiation of *endo*-$(\eta^3\text{-}C_3H_5)Fe(CO)_3Br$ in 3-methylpentane solution at 298 K. The positive peaks at 2087, 2041, and 2015 cm^{-1} correspond to *exo*-$(\eta^3\text{-}C_3H_5)Fe(CO)_3Br$. (b) IR difference spectral changes due to near-UV irradiation of *endo*-$(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$ in 3-methylpentane solution at 298 K. The positive peaks at 2107, 2055, and 2021 cm^{-1} correspond to *exo*-$(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$.

The sharp resonances in the ^1H NMR spectrum of $(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$ indicate that interconversion of the two conformational isomers is slow at room temperature. The ^1H NMR spectrum of $(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$ at 298 K resembles that of the $\eta^3\text{-}C_3H_5$ in $(\eta^3\text{-}C_3H_5)Mo(CO)_2(\eta^5\text{-}C_5H_5)$ at temperatures below 263 K.[3a] At 298 K the ^1H NMR for the $\eta^3\text{-}C_3H_5$ of $(\eta^3\text{-}C_3H_5)Mo(CO)_2(\eta^5\text{-}C_5H_5)$ shows only broad resonances signaling rapid interconversion of the exo and endo isomers. Therefore, the rate of interconversion of the isomers of $(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$ is much slower than that of $(\eta^3\text{-}C_3H_5)Mo(CO)_2(\eta^5\text{-}C_5H_5)$ at 298 K.

The IR spectrum of $(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$ in alkane solution at 298 K has three CO stretching bands (2109, 2060, 2016 cm^{-1}), which is consistent with $(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$ having a C_s symmetry. Evidently, the CO bands of *endo*-$(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$ obscure those of *exo*-$(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$.

(b) Endo-Exo Isomerization. Near-UV irradiation of $(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$ in alkane solutions at 298 K leads to spectral (IR and ^1H NMR) changes that are consistent with the interconversion represented by eq 1 (Figures 1 and

$$\textit{endo}\text{-}(\eta^3\text{-}C_3H_5)Ru(CO)_3Br \xrightarrow[\text{alkane}]{h\nu} \textit{exo}\text{-}(\eta^3\text{-}C_3H_5)Ru(CO)_3Br \quad (1)$$

2,Tables I and II). The ^1H NMR spectrum shows that the concentration of *exo*-$(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$ significantly increases upon photolysis (Figure 2). The resulting *exo*-$(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$ isomerizes thermally at 298 K to regenerate starting *endo*-$(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$ with a half-life greater than 10 min. This result supports our assertion that *endo*-$(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$ and *exo*-$(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$ are in thermal equilibrium and that *endo*-$(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$ is the thermodynamically more stable isomer.

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[12] Each doublet is actually a doublet of doublets. The geminal coupling of syn and anti protons is only about 1 Hz in both isomers.

[13] Syn and anti refer to the orientation of terminal allyl hydrogens relative to the central hydrogen. The syn hydrogen is on the same side of the C–C bond as the central hydrogen. Syn hydrogens are readily identified by their smaller coupling to the central hydrogen (8–10 Hz) compared with that of the anti hydrogens (13–15 Hz).

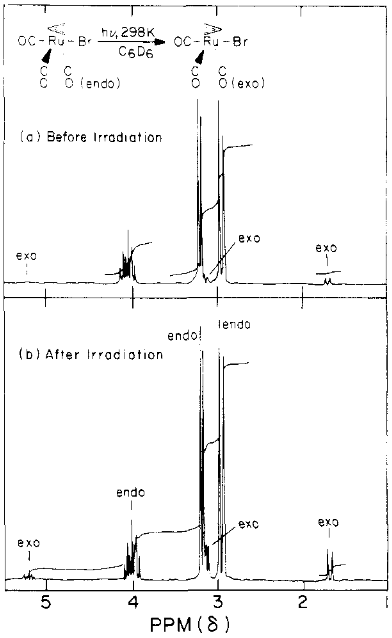

Figure 2. ^{1}H NMR spectral changes due to near-UV irradiation of (η^3-C_3H_5)Ru(CO)$_3$Br in C_6D_6 solution at 298 K (a) before irradiation and (b) after 30-s irradiation.

Further evidence for a rapid thermal equilibrium between *endo*-(η^3-C_3H_5)Ru(CO)$_3$Br and *exo*-(η^3-C_3H_5)Ru(CO)$_3$Br comes from following the course of the synthesis of (η^3-C_3H_5)Ru(CO)$_3$Br from reaction of Ru(CO)$_4$(C_2H_4) and C_3H_5Br. IR spectral changes consistent with the substitution reactions represented by eq 2 and 3 are observed following addition of allyl bromide at room temperature to an alkane solution of the substitutionally labile complex Ru(CO)$_4$(C_2H_4).[1] The difference IR spectrum shows that the three absorption bands in the CO stretching region for Ru(CO)$_4$(C_2H_4) decrease immediately after mixing and three new bands at 2108, 2053, and 2032 cm^{-1} increase in intensity. The IR spectrum of this new compound is similar to that of Ru(CO)$_4$(C_2H_4), and we assign the spectrum to Ru(CO)$_4$(η^2-C_3H_5Br). The positions of the three CO stretching bands for Ru(CO)$_4$(η^2-C_3H_5Br) are shifted to higher energy due to the electron-withdrawing bromine atom on the allyl group. It is possible that the transient product from allyl bromide and Ru(CO)$_4$(C_2H_4) is a direct oxidative addition product Ru(CO)$_4$Br(η^1-C_3H_5). However, the shift of the IR bands is seemingly too little to be consistent with this product. The transient species is too short-lived to characterize by NMR. The species formulated as Ru(CO)$_4$(η^2-C_3H_5Br) rapidly loses CO and oxidatively adds the carbon–bromine bond generating mainly *exo*-(η^3-C_3H_5)Ru(CO)$_3$Br. The reaction is complete within several minutes. The kinetic product *exo*-(η^3-C_3H_5)Ru(CO)$_3$Br then isomerizes to the thermodynamically more stable *endo*-(η^3-C_3H_5)Ru(CO)$_3$Br. The IR spectrum of *exo*-(η^3-C_3H_5)Ru(CO)$_3$Br in the CO stretching region is very similar to that of *endo*-(η^3-C_3H_5)Ru(CO)$_3$Br, as expected. The positions of the CO stretching bands differ by only 2–5 cm^{-1} for the two isomers (Figure 1b). This small difference explains why the small quantity of *exo*-(η^3-C_3H_5)Ru(CO)$_3$Br cannot be observed in the IR spectrum of the equilibrium mixture of (η^3-C_3H_5)Ru(CO)$_3$Br in 3-methylpentane at 298 K. The IR carbonyl stretching bands (Figure 1), which reveal the similarity between the two ruthenium isomers and the two iron isomers, further confirms our assignment of *endo*-(η^3-C_3H_5)Ru(CO)$_3$Br and *exo*-(η^3-C_3H_5)Ru(CO)$_3$Br.

$$\mathrm{Ru(CO)_4(C_2H_4)} + \mathrm{C_3H_5Br} \xrightarrow[\text{alkane}]{\Delta,\ 298\ \mathrm{K}} \mathrm{Ru(CO)_4(\eta^2\text{-}C_3H_5Br)} \quad (2)$$

$$\mathrm{Ru(CO)_4(\eta^2\text{-}C_3H_5Br)} \xrightarrow[\text{alkane}]{\Delta,\ 298\ \mathrm{K}} \textit{exo}\text{-}(\eta^3\text{-}\mathrm{C_3H_5})\mathrm{Ru(CO)_3Br} \quad (3)$$

(c) Low-Temperature Photochemistry of (η^3-C_3H_5)Ru(CO)$_3$Br. In order to understand the mechanism of the photochemical *endo*-*exo* rearrangement, it is necessary to determine the primary photoprocess. Consequently, we have studied the photochemistry of (η^3-C_3H_5)Ru(CO)$_3$Br in a low-temperature matrix. Near-UV irradiation of (η^3-C_3H_5)Ru(CO)$_3$Br in a 2-MeTHF glass at 77 K leads to spectral changes that are consistent with the loss of CO and presumably a weak complex with the solvent (eq 4). Importantly, formation of the exo isomer does not appear to compete with dissociative loss of CO from (η^3-C_3H_5)Ru(CO)$_3$Br. However, the CO bands in 2-MeTHF are somewhat broad, and the difference between exo and endo may not be detectable. The IR spectra show the generation of free CO (2132 cm^{-1}) and two new carbonyl stretching absorptions (2036, 1967 cm^{-1}) attributed to the 2-MeTHF adduct. Comparison of the decrease in intensity of the bands due to (η^3-C_3H_5)Ru(CO)$_3$Br with the increase in intensity of the band due to free CO shows that one molecule of CO is liberated for each molecule of (η^3-C_3H_5)Ru(CO)$_3$Br consumed.[14] The rigid glass precludes the diffusion of mononuclear intermediates, and this and the low concentration of (η^3-C_3H_5)Ru(CO)$_3$Br (1 mM) prevents formation of polynuclear species. Unfortunately, cooling alkane solutions of (η^3-C_3H_5)Ru(CO)$_3$Br leads to precipitation. This precludes study of the low-temperature photochemistry in the noncoordinating alkane solvents. If the 2-MeTHF glass containing (η^3-C_3H_5)Ru(CO)$_2$Br(2-MeTHF) is permitted to warm to room temperature, (η^3-C_3H_5)Ru(CO)$_2$Br(2-MeTHF) reverts quantitatively to (η^3-C_3H_5)Ru(CO)$_3$Br (eq 5). Unfortunately, the IR bands in 2-MeTHF are somewhat broader than in alkane, and we cannot unambiguously say whether the product in eq 5 is the endo or exo isomer.

$$(\eta^3\text{-}\mathrm{C_3H_5})\mathrm{Ru(CO)_3Br} \xrightarrow[\text{2-MeTHF}]{h\nu,\ 77\ \mathrm{K}} (\eta^3\text{-}\mathrm{C_3H_5})\mathrm{Ru(CO)_2(2\text{-}MeTHF)Br} + \mathrm{CO} \quad (4)$$

$$(\eta^3\text{-}\mathrm{C_3H_5})\mathrm{Ru(CO)_2Br(2\text{-}MeTHF)} + \mathrm{CO} \xrightarrow{\Delta} (\eta^3\text{-}\mathrm{C_3H_5})\mathrm{Ru(CO)_3Br} \quad (5)$$

(d) Spectroscopic Evidence for [(η^3-C_3H_5)Ru(CO)$_2$(μ-Br)]$_2$ as the Intermediate in the Photoisomerization of *endo*-(η^3-C_3H_5)Ru(CO)$_3$Br. Xenon flash (~50 μs) photolysis of (η^3-C_3H_5)Ru(CO)$_3$Br in 3-methylpentane solution at 298 K in a sealed NaCl IR cell followed by rapid acquisition (<5 s) of an FTIR spectrum (Figure 3) shows that a transient species A having two carbonyl stretching absorptions (2047, 1985 cm^{-1}) is formed prior to formation of *exo*-(η^3-C_3H_5)Ru(CO)$_3$Br. As shown in Figure 4, complex A reacts to give *exo*-(η^3-C_3H_5)Ru(CO)$_3$Br with a half-life on the order of 1 min for the conditions shown. The data in Figure 4 show that complex A does not yield *endo*-(η^3-C_3H_5)Ru(CO)$_3$Br. The data at least indicate the exo isomer to be generated with greater than 90% specificity. The *exo*-(η^3-C_3H_5)Ru(CO)$_3$Br isomerizes thermally to *endo*-(η^3-C_3H_5)Ru(CO)$_3$Br as discussed above. Intermediate A is not observed following irradiation of (η^3-C_3H_5)Ru(CO)$_3$Br in a solution saturated with CO. Importantly, endo to exo isomerization is not observed

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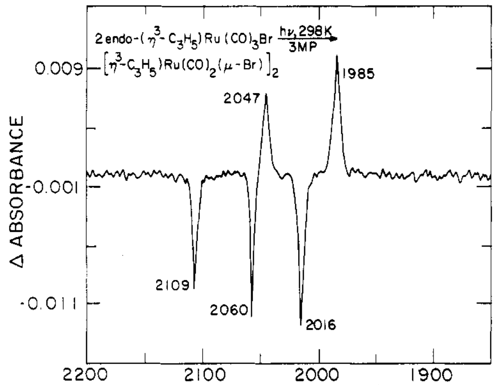


Figure 3. IR difference spectral changes due to near-UV irradiation of *endo*-$(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$ in 3-methylpentane solution at 298 K. The positive peaks at 2047 and 1985 cm^{-1} correspond to $[(\eta^3\text{-}C_3H_5)Ru(CO)_2(\mu\text{-}Br)]_2$.

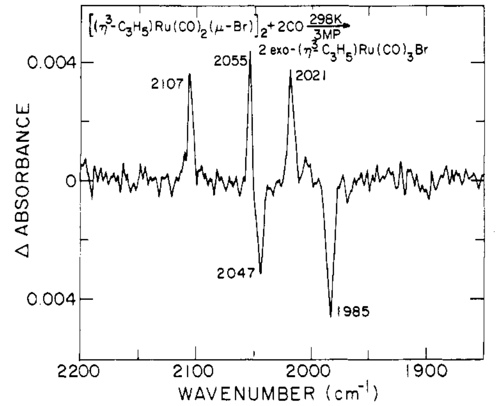


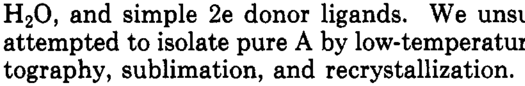
Figure 4. IR difference spectral changes accompanying the thermal reaction of $[(\eta^3\text{-}C_3H_5)Ru(CO)_2(\mu\text{-}Br)]_2$ which is the same sample in Figure 3 in 3-methylpentane at 298 K (Δ = 1 min). The positive peaks at 2107, 2055, and 2021 cm^{-1} correspond to *exo*-$(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$.

under CO, suggesting that intermediate A is crucial to the photoisomerization. However, vigorously purging a solution of $(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$ with Ar during photolysis results in the accumulation of A. Complex A is stable for at least 1 h in alkane solution under an inert atmosphere at 298 K. Photolysis of $(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$ was usually stopped at about 50% conversion to avoid secondary photoreactions of complex A.

Complex A is susceptible to thermal reaction with O_2, H_2O, and simple 2e donor ligands. We unsuccessfully attempted to isolate pure A by low-temperature chromatography, sublimation, and recrystallization. We have, however, characterized A spectroscopically (mass, ^{1}H NMR, and IR) as the dibromo-bridged dimer $[(\eta^3\text{-}C_3H_5)Ru(CO)_2(\mu\text{-}Br)]_2$ in samples containing unreacted $(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$ (eq 6). This chemistry is quite similar

$$2(\eta^3\text{-}C_3H_5)Ru(CO)_3Br \xrightarrow[\text{Ar-purged alkane}]{h\nu,\ 298\ K} [(\eta^3\text{-}C_3H_5)Ru(CO)_2(\mu\text{-}Br)]_2 + 2\ CO \quad (6)$$

to that for complexes $M(CO)_5X$ (M = Mn, Re; X = Cl, Br, I) (eq 7).[15] Of course, many other dihalo-bridged com-


$$2M(CO)_5X \xrightarrow[\text{alkane}]{\Delta \text{ or } h\nu} (CO)_4M(\mu\text{-}X)_2M(CO)_4 + 2CO \quad (7)$$

plexes are known including $[M(CO)_3X_2]_2$[16] (M = Ru, Os; X = Cl, Br, I) and $[M(C_3H_5)_2X]_2$[17] (M = Ni, Pd, Pt; X = Cl, Br, I). The field-desorption mass spectrum of the solid obtained from evaporating alkane solvent from an irradiated solution of $(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$ shows a parent peak at *m/z* 558 having the same isotopic pattern as predicted for the dibromo-bridged dimer $Ru_2C_{10}H_{10}O_2Br_2$ and a parent peak at *m/z* 325 for the unreacted starting material. The IR spectrum shows only two terminal CO stretching bands which indicates that two pairs of the four carbonyls in $[(\eta^3\text{-}C_3H_5)Ru(CO)_2(\mu\text{-}Br)]_2$ are equivalent and that the complex is not bridged by CO. The absence of an IR band near 1640 cm^{-1} suggests that the allyl group in $[(\eta^3\text{-}C_3H_5)Ru(CO)_2(\mu\text{-}Br)]_2$ is still π-coordinated to Ru.[18] The ^{1}H NMR spectra of mixtures of $(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$ and $[(\eta^3\text{-}C_3H_5)Ru(CO)_2(\mu\text{-}Br)]_2$ in $CDCl_3$ and in C_6D_6 show new resonances attributable to $[(\eta^3\text{-}C_3H_5)Ru(CO)_2(\mu\text{-}Br)]_2$, but the resonances are broad and not useful in characterizing the complex. The broadness of the bands in the IR spectrum and of the resonances in the ^{1}H NMR spectrum of $[(\eta^3\text{-}C_3H_5)Ru(CO)_2(\mu\text{-}Br)]_2$ is possibly caused by presence of several isomers (e.g. exo–exo, exo–endo, and endo–endo).

Reaction of $[(\eta^3\text{-}C_3H_5)Ru(CO)_2(\mu\text{-}Br)]_2$ with 2e donor ligands occurs thermally as shown in eq 8. The complex

$$[(\eta^3\text{-}C_3H_5)Ru(CO)_2(\mu\text{-}Br)]_2 + L \xrightarrow[\text{alkane}]{\Delta,\ 298\ K} (\eta^3\text{-}C_3H_5)Ru(CO)_2(L)Br \quad (8)$$

$[(\eta^3\text{-}C_3H_5)Ru(CO)_2(\mu\text{-}Br)]_2$ reacts rapidly at room temperature with CO (1 atm) or PPh_3 giving the substituted mononuclear ruthenium complexes (eq 8). Interestingly, $[(\eta^3\text{-}C_3H_5)Ru(CO)_2(\mu\text{-}Br)]_2$ does not react with C_2H_4 (1 atm) or with Et_3SiH at 298 K, ruling out the intermediacy of the dimer in the 298 K photochemical reactions of $(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$ in the presence of C_2H_4 or Et_3SiH (vide infra).

(e) Crossover-Product Evidence for a Dibromo-Bridged Dimer Intermediate. A crossover experiment provides the crucial evidence that $[(\eta^3\text{-}C_3H_5)Ru(CO)_2(\mu\text{-}Br)]_2$ has a dihalo-bridged dimer structure and can be an intermediate in the photoisomerization of *endo*-$(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$. Irradiation a solution of 0.5 mM $(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$ and 0.5 mM $(\eta^3\text{-}2\text{-methylallyl})Ru(CO)_3Cl$ in C_6D_{12} at room temperature leads to ^{1}H NMR spectral changes (Table III) that are consistent with the crossover reaction represented by eq 9. In the ^{1}H NMR spectrum

$$(\eta^3\text{-}C_3H_5)Ru(CO)_3Br + (\eta^3\text{-}2\text{-methylallyl})Ru(CO)_3Cl \xrightarrow[\text{alkane}]{h\nu,\ 298\ K} (\eta^3\text{-}2\text{-methylallyl})Ru(CO)_3Br + (\eta^3\text{-}C_3H_5)Ru(CO)_3Cl \quad (9)$$

measured after irradiation, we observe that resonances due to $(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$ and $(\eta^3\text{-}2\text{-methylallyl})Ru(CO)_3Cl$ have decreased and that two net sets of resonances have increased in intensity. One set has three singlets in the ratio of 2:2:3 and is assigned to $(\eta^3\text{-}2\text{-methylallyl})Ru(CO)_3Br$. The second set has a multiplet and two doublets in the ratio of 1:2:2 and is assigned to $(\eta^3\text{-}C_3H_5)Ru(CO)_3Cl$

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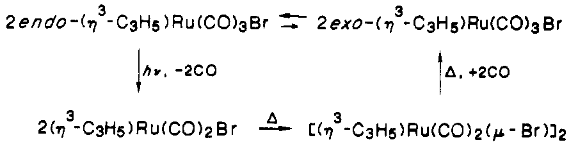
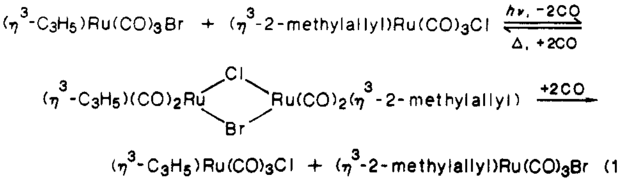
Scheme I. Photochemistry of (η^3-C_3H_5)Ru(CO)$_3$Br in Alkane Solution



which has been independently prepared. The quantities of crossover products generated are the same, from integration of the ^{1}H NMR. The chloro–bromo-bridged ruthenium species is the logical precursor to the crossover products (eq 10).



(10)

We summarize the photochemistry of (η^3-C_3H_5)Ru(CO)$_3$Br in alkane solution at 298 K in the absence of any added ligands in Scheme I. The analogous Fe complex (η^3-C_3H_5)Fe(CO)$_3$Br has not been studied in detail. However, the preliminary results show that the Fe complex has the same photochemistry as observed for (η^3-C_3H_5)Ru(CO)$_3$Br except the rate of exo–endo isomerization is much faster for (η^3-C_3H_5)Fe(CO)$_3$Br (Figure 1a, Tables I and II).

(f) Reactivity of (η^3-C_3H_5)Ru(CO)$_2$Br. The observation of (η^3-C_3H_5)Ru(CO)$_2$(2-MeTHF)Br during photolysis of (η^3-C_3H_5)Ru(CO)$_3$Br in a 2-MeTHF matrix suggests that (η^3-C_3H_5)Ru(CO)$_2$Br is an intermediate in the conversion of (η^3-C_3H_5)Ru(CO)$_3$Br to [(η^3-C_3H_5)Ru(CO)$_2$(μ-Br)]$_2$ during irradiation of (η^3-C_3H_5)Ru(CO)$_3$Br in alkane solutions at 298 K. The photogenerated 16e species (η^3-C_3H_5)Ru(CO)$_2$Br is too reactive to observe spectroscopically at 298 K using steady-state methods. However, when the irradiation is carried out in hydrocarbon solvents containing PPh$_3$ or C_2H_4, IR and ^{1}H NMR data show that (η^3-C_3H_5)Ru(CO)$_2$Br can be trapped (eq 11). Irradiation of (η^3-C_3H_5)Ru(CO)$_3$Br at 313 nm in alkane solution at 298 K in the presence of 0.05 M PPh$_3$ rapidly yields (η^3-C_3H_5)Ru(CO)$_2$(PPh$_3$)Br (Φ = 0.7) having two CO stretching bands at 2044 and 1978 cm^{-1}. The positions of the bands in the IR are the same as the literature values for (η^3-C_3H_5)Ru(CO)$_2$(PPh$_3$)Br.[18b] The compound has been further characterized by mass spectrometry and ^{1}H NMR. Successive decarbonylation and loss of the π-allyl group are observed in the EI mass spectrum of (η^3-C_3H_5)Ru(CO)$_2$(PPh$_3$)Br, but no parent peak is observed for (η^3-C_3H_5)Ru(CO)$_2$(PPh$_3$)Br. However, the field-desorption mass spectrum shows a parent peak at *m/z* 542 having the same isotopic pattern as predicted for (η^3-C_3H_5)Ru(CO)$_2$(PPh$_3$)Br. The phosphine in (η^3-C_3H_5)Ru(CO)$_2$(PPh$_3$)Br is probably cis to the bromine atom since the ^{1}H NMR spectrum shows an AA′MM′X pattern for the π-allyl group.

$$(\eta^3\text{-}C_3H_5)Ru(CO)_2Br + L \xrightarrow{\Delta} (\eta^3\text{-}C_3H_5)Ru(CO)_2(L)Br \qquad (11)$$

$$L = PPh_3,\ C_2H_4$$

Irradiation of (η^3-C_3H_5)Ru(CO)$_3$Br in C_2H_4-saturated alkane solution yields (η^3-C_3H_5)Ru(CO)$_2$(C_2H_4)Br which has two terminal carbonyl absorptions at 2072 and 1992 cm^{-1} for (η^3-C_3H_5)Ru(CO)$_2$(C_2H_4)Br. The ^{1}H NMR spectrum of (η^3-C_3H_5)Ru(CO)$_2$(C_2H_4)Br also shows an AA′MM′X pattern for the π-allyl group which indicates the C_2H_4 ligand cis to the bromine atom. In contrast, (η^3-C_3H_5)Ru(CO)$_3$Cl reacts with C_2H_4 at 353 K yielding [Ru(COC$_2H_5$)(CO)$_2$Cl]$_n$.[19] The C_2H_4 of (η^3-C_3H_5)Ru(CO)$_2$(C_2H_4)Br can be easily replaced by PPh$_3$ by thermal reaction upon addition of PPh$_3$ at 298 K to an alkane solution of (η^3-C_3H_5)Ru(CO)$_2$(C_2H_4)Br to form (η^3-C_3H_5)Ru(CO)$_2$(PPh$_3$)Br. We note that under reduced pressure at 298 K, (η^3-C_3H_5)Ru(CO)$_2$(C_2H_4)Br loses C_2H_4 and forms the dibromo-bridged dimer [(η^3-C_3H_5)Ru(CO)$_2$(μ-Br)]$_2$. The complex [(η^3-C_3H_5)Ru(CO)$_2$(μ-Br)]$_2$ does not react with C_2H_4 at 1 atm and 298 K. This is the result which indicates that [(η^3-C_3H_5)Ru(CO)$_2$(μ-Br)]$_2$ is not an intermediate in the photochemical reaction of C_2H_4 and (η^3-C_3H_5)Ru(CO)$_3$Br.

Triethylsilane also reacts with (η^3-C_3H_5)Ru(CO)$_2$Br by oxidative addition involving the Si–H bond to form (η^3-C_3H_5)Ru(CO)$_2$(H)(SiEt$_3$)Br. The IR spectrum shows two new bands at 2047 and 2008 cm^{-1} after photolysis of (η^3-C_3H_5)Ru(CO)$_3$Br in alkane solution at room temperature in the presence of excess triethylsilane. The ^{1}H NMR spectrum of this reaction mixture in C_6D_6 shows a resonance characteristic of metal hydride at −10.5 ppm.

Spectral data show that the structure of (η^3-C_3H_5)Ru(CO)$_3$Br is similar to that of (η^3-C_3H_5)Fe(CO)$_3$Br. The complex (η^3-C_3H_5)Ru(CO)$_3$Br is a pseudooctahedral and has one CO ligand trans to the bromine and the other two CO ligands cis to the bromine. The ^{1}H NMR spectra of the photosubstitution products (η^3-C_3H_5)Ru(CO)$_2$(L)Br (L = PPh$_3$, C_2H_4) show that the ligand L is cis to the bromine. We have also obtained results which show that irradiation of (η^3-C_3H_5)Ru(CO)$_3$Br in the presence of ^{13}CO results in incorporation of ^{13}CO into a position cis to the bromine. These results are consistent with, but do not prove, that a cis CO ligand is lost upon photolysis.

Flash photolysis of (η^3-C_3H_5)Ru(CO)$_3$Br in 3-methylpentane solution saturated with ^{13}CO at 298 K produces three new CO stretching bands at 2097, 2034, and 2008 cm^{-1} in the IR spectrum. The positions of the absorptions are identical with the three of the four weak absorptions observed in a concentrated solution of (η^3-C_3H_5)Ru(CO)$_3$Br which can be attributed to natural-abundance (η^3-C_3H_5)Ru(CO)$_2$(^{13}CO)Br. We therefore assign the structure of the photoproduct to (η^3-C_3H_5)Ru(CO)$_2$(^{13}CO)Br. The force-field method,[20] which neglects coupling between CO stretching modes and other molecular vibrations, was used to calculate the force constants for CO stretching (K_{cis} and K_{trans}) and the force constant for interaction between the CO ligands (K_i) of (η^3-C_3H_5)Ru(CO)$_3$Br. The Ru(CO)$_3$ fragment has four CO force constants, K_{cis} and K_{trans}, and the two interaction force constants, $K_{cis,cis}$ and $K_{trans,cis}$. As previously assumed[21] we take $K_{cis,cis} = K_{trans,cis}$. The values for K_{cis}, K_{trans}, and K_i are 1747, 1658, and 33 N m^{-1}, respectively. We used these force constants to predict the frequencies for the axial and equatorial ^{13}CO-substituted products. The calculated CO stretching frequencies for (η^3-C_3H_5)Ru(CO)$_2$(^{13}CO)$_{cis}$Br are in good agreement (±1 cm^{-1}) with the experimental frequencies for (η^3-C_3H_5)Ru(CO)$_2$(^{13}CO)$_{cis}$Br (Table II). The photochemistry of (η^3-C_3H_5)Ru(CO)$_3$Br in alkane solution at 298 K in the presence of reactive molecules is summarized in Scheme II.

Conclusions

We have shown that two isomers of (η^3-C_3H_5)Ru(CO)$_3$Br differing principally in the orientation of the allyl group

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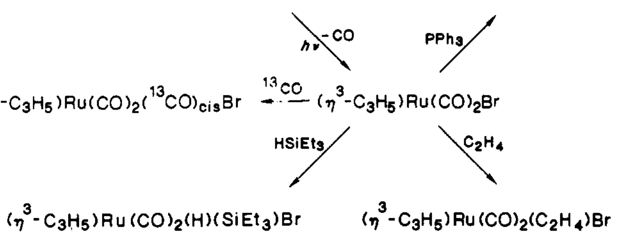
Scheme II. Photochemistry of (η^3-C_3H_5)Ru(CO)$_3$Br in Alkane Solution at 298 K Containing Reactive Molecules



exist in equilibrium in solution. *endo*-(η^3-C_3H_5)Ru(CO)$_3$Br is more stable than *exo*-(η^3-C_3H_5)Ru(CO)$_3$Br by about 2 kcal/mol. Photolysis shifts the equilibrium toward *exo*-(η^3-C_3H_5)Ru(CO)$_3$Br. The dibromo-bridged ruthenium dimer [(η^3-C_3H_5)Ru(CO)$_2$(μ-Br)]$_2$ is the dominant intermediate in the photoinduced endo–exo isomerization. Photolysis of (η^3-C_3H_5)Ru(CO)$_3$Br in the presence of CO does not yield significant endo → exo isomerization. Without detailed structural information, it is difficult to speculate why [(η^3-C_3H_5)Ru(CO)$_2$(μ-Br)]$_2$ and CO yield *exo*-(η^3-C_3H_5)Ru(CO)$_3$Br rather than *endo*-(η^3-C_3H_5)Ru(CO)$_3$Br. However, we note that the two allyl ligands of [(η^3-C_3H_5)Fe(CO)$_3$]$_2$ are both in exo positions even though the precursor (η^3-C_3H_5)Fe(CO)$_3$X (X = Br, I) has the endo structure.[6-7,11] Further attempts to isolate and structurally characterize of [(η^3-C_3H_5)Ru(CO)$_2$(μ-Br)]$_2$ are underway.

Interestingly, the allyl group remains π-coordinated to ruthenium in all of the products obtained from photolysis of (η^3-C_3H_5)Ru(CO)$_3$Br. In contrast, thermal reactions of (η^3-C_3H_5)Ru(CO)$_3$Cl typically result in σ-allyl complexes.[18b] This difference might be due to the fact that CO loss is the primary photoprocess, while π-allyl conversion to σ-allyl is believed to be the primary thermal process.[18a] Photolysis provides a useful route to (η^3-C_3H_5)Ru(CO)$_2$(L)Br complexes.

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Registry No. [(η^3-C_3H_5)Ru(CO)$_2$Br]$_2$, 114860-57-0; (η^3-C_3H_5)Ru(CO)$_2$(PPh$_3$)Br, 114925-32-5; (η^3-C_3H_5Ru(CO)$_2$(C_2H_4Br, 114860-58-1; (η^3-C_3H_5)Ru(CO)$_3$Br, 114925-33-6; PPh$_3$, 603-35-0; C_2H_4, 74-85-1; *endo*-(η^3-C_3H_5)Ru(CO)$_3$Br, 114925-34-7; *exo*-(η^3-C_3H_5)Ru(CO)$_3$Br, 114925-35-8; *endo*-(η_3-H_5)Fe(CO)$_3$Br, 61216-85-1; *exo*-(η^3-C_3H_5)Fe(CO)$_3$Br, 80797-22-4; (η^3-C_3H_5)Ru(CO)$_2$(2-MeTHF)Br, 114860-59-2; (η_3-C_3H_5)Ru(CO)$_2$CH)(SiEt$_3$)Br, 114860-60-5; (η^3-C_3H_5)Ru(CO)$_2$(^{13}CO)$_{cis}$Br, 114860-61-6; (η^3-C_3H_5)Ru(CO)$_2$(^{13}CO)$_{trans}$Br, 114925-36-9; Ru(CO)$_4$(C_2H_4e, 52621-15-5; (η^3-C_3H_5)Ru(CO)$_3$Cl, 114925-37-0; (η^3-C_4H_7)Ru(CO)$_3$Br, 114860-62-7; (η^3-C_4H_7)Ru(CO)$_3$Cl, 114925-38-1; [(η^3-C_3H_5)Fe(CO)$_2$Br]$_2$, 114860-63-8.

Binuclear Bis(dimethylphosphino)methane Complexes of Rhodium and Some Comparisons with the Bis(diphenylphosphino)methane Analogues of Rhodium and Iridium

James A. Jenkins, Jimmy P. Ennett, and Martin Cowie*

Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2

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The reaction of bis(dimethylphosphino)methane (DMPM = $Me_2PCH_2PMe_2$) with [RhCl(C_8H_{12})]$_2$ under CO yields the binuclear complex *trans*-[RhCl(CO)(DMPM)]$_2$ (1), which upon reaction with either 1 equiv of AgBF$_4$ or an excess of $Na_2S\cdot 9H_2O$ yields the A-frame complexes [Rh$_2$(CO)$_2$(μ-Cl)(DMPM)$_2$][BF$_4$] or [Rh$_2$(CO)$_2$(μ-S)(DMPM)$_2$], respectively. In solution under a CO atmosphere the cationic, chloride-bridged species was found to be in equilibrium with the symmetrical tricarbonyl compound [Rh$_2$(CO)$_2$(μ-Cl)(μ-CO)(DMPM)$_2$][BF$_4$]. The additional carbonyl ligand in this complex is found to be more labile than that in the analogous "Rh$_2$(DPPM)$_2$" and "Ir$_2$(DPPM)$_2$" systems (DPPM = bis(diphenylphosphino)methane). This has been confirmed for the rhodium species by NMR magnetization transfer experiments. Under higher concentrations of CO a labile species, believed to be the tetracarbonyl [Rh$_2$Cl(CO)$_3$(μ-CO)(DMPM)$_2$]$^+$, is observed. The neutral A-frame [Rh$_2$(CO)$_2$(μ-S)(DMPM)$_2$] also reacts with CO to yield the labile tetracarbonyl species [Rh$_2$(CO)$_4$(μ-S)(DMPM)$_2$]. Addition of 1 equiv of the activated alkynes dimethyl acetylenedicarboxylate (DMA) or hexafluorobutyne (HFB) to 1 in solution provides the cis-dimetalated olefin species [Rh$_2$Cl$_2$(CO)$_2$(μ-RC$_2$R)(DMPM)$_2$] (R = CO$_2$CH$_3$, CF$_3$). Subsequent reaction of these products with 1 equiv of AgBF$_4$ yields the cationic species [Rh$_2$Cl(CO)$_2$(μ-RC$_2$R)(DMPM)$_2$][BF$_4$], both of which are found to be fluxional on the NMR time scale. These latter two complexes are also synthesized by the addition of 1 equiv of DMA or HFB to [Rh$_2$(CO)$_2$(μ-Cl)(DMPM)$_2$][BF$_4$]. Compound 1 reacts with CH_2Cl_2 over an extended period of time yielding the tetrachloride product [RhCl$_2$(CO)(DMPM)]$_2$ which can also be obtained by reaction of 1 with HCl or Cl$_2$. The structure of this Cl$_2$ adduct was determined by X-ray techniques. It crystallizes in the orthorhombic space group *Pbcn* with a = 30.573 (4) Å, b = 13.469 (2) Å, c = 12.624 (2) Å, V = 5198.8 Å^3, and Z = 8. The structure was refined to R = 0.044 and R_w = 0.058 based on 3985 unique observed reflections and 239 variables. The structure has a Rh–Rh separation of 2.7591 (5) Å corresponding to a normal single bond. Each rhodium atom exhibits octahedral coordination in which the ligands on each metal are staggered with regard to each other about the Rh–Rh bond with an average torsion angle of 22.0°. The two Rh–Cl bonds opposite the Rh–Rh bond (2.480 (1), 2.478 (1) Å) are significantly longer than those cis to this bond (2.385 (1), 2.393 (1) Å).

Introduction

Much of the interest in binuclear complexes arises from the possibility that the two adjacent metals may interact in a cooperative manner with substrate molecules and in so doing may result in reactivity modes that differ from those displayed by mononuclear complexes. In any system

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