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Thermal Reactions of $Ru(CO)_3(C_2H_4)_2$ with Acyclic, Nonconjugated Dienes and Photochemistry of $Ru(CO)_4(\eta^2\text{-diene})$ Complexes

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Near-UV irradiation of $Ru(CO)_4(\eta^2\text{-1,4-pentadiene})$, formed from visible-light ($\lambda > 420$ nm) irradiation of $Ru_3(CO)_{12}$, in alkane solution containing excess 1,4-pentadiene at 298 K yields $Ru(CO)_3(\eta^4\text{-1,4-pentadiene})$ even in the presence of ~1 M 1,4-pentadiene. The complex $Ru(CO)_3(\eta^4\text{-1,4-pentadiene})$ isomerizes to the thermodynamically more stable conjugated diene complex $Ru(CO)_3(\eta^4\text{-1,3-pentadiene})$ with a half-time of about 2 min at 298 K. Near-UV irradiation of $Ru(CO)_4(\eta^2\text{-1,4-pentadiene})$ in rigid methylcyclohexane glasses containing ~1 M 1,4-pentadiene at 77 K yields $Ru(CO)_3(\eta^4\text{-1,4-pentadiene})$ as the major product (~75%), but $HRu(CO)_3(\eta^3\text{-}C_5H_7)$ is also observed as a minor product (~25%) that isomerizes to $Ru(CO)_3(\eta^4\text{-1,3-pentadiene})$ above 198 K. Room temperature photolysis of $Ru(CO)_4(\eta^2\text{-3-methyl-1,4-pentadiene})$ in the presence of 3-methyl-1,4-pentadiene gives $Ru(CO)_3(\eta^4\text{-3-methyl-1,4-pentadiene})$, and this species reacts to give a 1,3-diene complex with a half-time of >3 h. Near-UV irradiation of $Ru(CO)_4(\eta^2\text{-1,5-hexadiene})$ in the presence of ~1 M 1,5-hexadiene yields the nonconjugated diene complex $Ru(CO)_3(\eta^4\text{-1,5-hexadiene})$. In contrast to $Ru(CO)_3(\eta^4\text{-1,4-pentadiene})$, $Ru(CO)_3(\eta^4\text{-1,5-hexadiene})$ is stable for hours in alkane solution at 298 K. Near-UV irradiation of $Ru(CO)_4(\eta^2\text{-1,6-heptadiene})$ in the presence of ~1 M 1,6-heptadiene does not generate a chelating diene complex $Ru(CO)_3(\eta^4\text{-1,6-heptadiene})$ but rather the bis(olefin) complex $Ru(CO)_3(\eta^2\text{-1,6-heptadiene})_2$. Thermal reaction of $Ru(CO)_3(C_2H_4)_2$ with ~1 M diene = 1,4-pentadiene, 3-methyl-1,4-pentadiene, 1,5-hexadiene, and 1,6-heptadiene yields the same products as observed from photolysis of $Ru(CO)_4(\eta^2\text{-diene})$ in ~1 M diene at 298 K.

We wish to report the photochemistry of $Ru(CO)_4(\eta^2\text{-diene})$ (diene = 1,4-pentadiene, 3-methyl-1,4-pentadiene, 1,5-hexadiene, 1,6-heptadiene) complexes and the thermal reaction of $Ru(CO)_3(C_2H_4)_2$ with these dienes. We[1–4] and others[5–9] have previously reported the photochemical generation of catalytic intermediates at low temperatures as a means of investigating reactions of alkene complexes. In particular, we examined the photoassisted alkene isomerization catalysts derived from $Fe(CO)_5$ and $Ru_3(CO)_{12}$.[10–13] The key intermediate, $HM(CO)_3(\eta^3\text{-}C_3H_5)$, can be observed spectroscopically in a low-temperature matrix.[1,4] However, the absence of synthetic routes to $M(CO)_n$(nonconjugated diene) complexes has hindered mechanistic studies of transition-metal carbonyl catalyzed isomerization of nonconjugated dienes. An attempted synthesis that we tried, near-UV irradiation of an alkane solution of $Ru_3(CO)_{12}$ and 1,4-pentadiene, yields $Ru(CO)_3$(1,3-pentadiene) without buildup of the intermediate(s). $Ru(CO)_3$(1,5-cyclooctadiene) undergoes reaction with 1,4-pentadiene at 100 °C to give directly $Ru(CO)_3$(1,3-pentadiene).[14] Thus, both pathways to form pentadiene complexes yield isomerization of the 1,4-diene to give a conjugated diene complex.

Here, we report the use of $Ru(CO)_3(C_2H_4)_2$[1] as a "$Ru(CO)_3$"-transfer reagent permitting preparation of the new, thermally labile complexes $Ru(CO)_3(\eta^4\text{-1,4-pentadiene})$, $Ru(CO)_3(\eta^4\text{-3-methyl-1,4-pentadiene})$, and $Ru(CO)_3(\eta^4\text{-1,5-hexadiene})$, eq 1. The η^4-diene complexes are reactive. For example,

$$Ru(CO)_3(C_2H_4)_2 + \text{diene} \xrightarrow{298\ \text{K}} Ru(CO)_3(\eta^4\text{-diene}) + 2C_2H_4 \quad (1)$$

$Ru(CO)_3(\eta^4\text{-1,4-pentadiene})$ isomerizes rapidly at 298 K to $Ru(CO)_3(\eta^4\text{-1,3-pentadiene})$ probably via $Ru(CO)_3(\eta^2\text{-1,4-pentadiene})$. The complexes $Ru(CO)_3(\eta^4\text{-1,4-pentadiene})$, $Ru(CO)_3(\eta^4\text{-3-methyl-1,4-pentadiene})$, and $Ru(CO)_3(\eta^4\text{-1,5-hexadiene})$ can also be obtained by near-UV irradiation of $Ru(CO)_4(\eta^2\text{-diene})$ in alkane solution at 298 K. The $Ru(CO)_4(\eta^2\text{-diene})$ complexes can be cleanly made with excess diene via visible-light ($\lambda > 420$ nm) photolysis of $Ru_3(CO)_{12}$ where $Ru(CO)_4(\eta^2\text{-diene})$ does not absorb, eq 2.

$$Ru_3(CO)_{12} + 3(\text{diene}) \xrightarrow{h\nu} 3Ru(CO)_4(\eta^2\text{-diene}) \quad (2)$$

Experimental Section

Materials. All solvents were reagent grade and freshly distilled before use. The $Ru_3(CO)_{12}$ was obtained from Strem Chemicals and was used as received. The photochemistry at low temperature was carried out by using methylcyclohexane (J. T. Baker) as the matrix material. 1,3-Pentadiene, 1,4-pentadiene, 3-methyl-1,4-pentadiene, 1,5-hexadiene, and 1,6-heptadiene were obtained from Aldrich and passed through Al_2O_3 prior to use. Research grade C_2H_4 was obtained from Matheson. PPh_3 was recrystallized prior to use.

Instrumentation. IR spectra were recorded on a Nicolet 7199 or 60SX Fourier transform IR spectrometer. ^1H NMR spectra were recorded on a Varian 300 MHz Fourier transform spectrometer. UV–vis spectra were recorded with a Hewlett-Packard 8451A diode array spectrometer. Gas chromatograph–mass spectra (GC-MS) were recorded on a Hewlett-Packard Model 5992 mass spectrometer. All mass spectra were recorded at 70 eV. Separations were done by using a 10 ft × $^1/_8$ in. SE-30 on Chromasorb W column. A Model A high-energy micropulser 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.

Procedures. Generally, all manipulations were carried out under N_2 in a Vacuum Atmospheres drybox or under Ar by using conventional Schlenk-line techniques. Low-temperature irradiations involved the use of a Bausch & Lomb SP200 200-W high-pressure Hg lamp filtered with a 10-cm Pyrex water filter. Low-temperature IR spectra were recorded by using a Precision Cell, Inc., Model P/N 21.000 variable-temperature cell equipped with CaF_2 windows.

Solutions of ~1 mM $Ru(CO)_3(C_2H_4)_2$ were prepared according to the literature procedure,[1] and all solutions of $Ru(CO)_3(C_2H_4)_2$ were saturated with C_2H_4 to prevent decomposition. In a typical procedure, the $Ru(CO)_4(C_2H_4)$ was prepared quantitatively via visible-light ($\lambda > 420$ nm) irradiation of 0.4 mM $Ru_3(CO)_{12}$ in a continuously C_2H_4-purged alkane solution using a filtered Hanovia 550-W medium-pressure Hg lamp. The $Ru(CO)_3(C_2H_4)_2$ solution was prepared by subsequent near-UV irradiation of a $Ru(CO)_4(C_2H_4)$ solution at 298 K in the presence of C_2H_4. Only $Ru(CO)_4(C_2H_4)$ and $Ru(CO)_3(C_2H_4)_2$ were

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Table I. IR Data for Relevant Complexes

species	medium (T, K)	ν, cm^{-1} (rel abs)
$Ru_3(CO)_{12}$	3MP[a] (298)	2061 (2.7), 2031 (1.6), 2012 (1.0)
$Ru(CO)_3(PPh_3)_2$	3MP (298)	1907
$Ru(CO)_3(C_2H_4)$[c]	3MP (55)	2055 (1.0), 1978 (1.2), 1972 (1.3)
$Ru(CO)_4(C_2H_4)$	3MP (298)	2104 (1.0), 2023 (17.2), 1996 (8.5)
$Ru(CO)_4(C_3H_6)$	3MP (298)	2100 (1.0), 2018 (10.6), 1991 (6.4)
$Ru(CO)_4(C_5H_{10})$	3MP (298)	2100 (1.0), 2018 (9.3), 1989 (5.8)
$Ru(CO)_4(\eta^2$-1,4-pentadiene)	3MP (298)	2101 (1.0), 2019 (9.5), 1994 (5.1)
	MCH[b] (298)	2101 (1.0), 2019 (10.7), 1993 (6.0)
	MCH (77)	2103 (1.0), 2020 (7.0), 1991 (5.4)
$Ru(CO)_4(\eta^2$-3-methyl-$C_5H_7)$[d]	3MP (298)	2101 (1.0), 2019 (9.1), 1993 (4.9)
$Ru(CO)_4(\eta^2$-1,5-hexadiene)	3MP (298)	2101 (1.0), 2019 (9.2), 1992 (5.0)
$Ru(CO)_4(\eta^2$-1,6-heptadiene)	3MP (298)	2100 (1.0), 2019 (9.6), 1992 (4.8)
$Ru(CO)_3(C_2H_4)_2$	3MP (298)	2081 (1.0), 2005 (7.1), 1995 (20.3)
$Ru(CO)_3(C_3H_6)_2$	3MP (298)	2075 (1.0), 2005 (3.3), 1988 (14.0)
$Ru(CO)_3(C_5H_{10})_2$	3MP (298)	2072 (1.0), 2005 (2.6), 1987 (9.4)
$Ru(CO)_3(\eta^2$-1,4-pentadiene$)_2$	MCH (77)	2077 (1.0), 2002 (3.0), 1994 (6.1)
$Ru(CO)_3(\eta^2$-1,6-heptadiene$)_2$	3MP (298)	2074 (1.0), 1998 (2.5), 1986 (9.8)
$Ru(CO)_3(\eta^4$-1,4-pentadiene)	3MP (298)	2050 (1.1), 1992 (1.0), 1966 (1.0)
	MCH (77)	2048 (1.0), 1992 (1.0), 1960 (1.1)
$Ru(CO)_3(\eta^4$-3-methyl-1,4-$C_5H_7)$[d]	3MP (298)	2052 (1.2), 1994 (1.1), 1968 (1.0)
$Ru(CO)_3(\eta^4$-1,5-hexadiene)	3MP (298)	2050 (1.1), 1994 (1.1), 1966 (1.0)
$Ru(CO)_3(\eta^4$-1,3-pentadiene)	3MP (298)	2063 (1.0), 1998 (1.6), 1987 (1.4)
$Ru(CO)_3(\eta^4$-3-methyl-1,3-$C_5H_7)$[e]	3MP (298)	2061 (1.0), 1996 (1.5), 1983 (1.4)
$Ru(CO)_3(\eta^4$-1,3-butadiene)[f]	hexane (298)	2069 (s), 2006 (vs), 1995 (s)
$HRu(CO)_3(\eta^3$-$C_3H_5)$	MCH (77)	2082 (1.0), 2008 (1.2)
$HRu(CO)_3(\eta^3$-$C_5H_9)$	MCH (77)	2078 (1.0), 2004 (1.2)
$HRu(CO)_3(\eta^3$-$C_5H_7)$	MCH (77)	2080 (1.0), 2006 (1.2)

[a] 3MP = 3-methylpentane. [b] MCH = methylcyclohexane. [c] Band positions obtained from ref 1. [d] 3-methyl-1,4-C_5H_7 = 3-methyl-1,4-pentadiene. [e] 3-methyl-1,3-C_5H_7 = 3-methyl-1,3-pentadiene. [f] Band positions obtained from ref 14.

spectroscopically detected in these solutions. After ~90% conversion of $Ru(CO)_4(C_2H_4)$, the photolysis was stopped and the solution was purged with C_2H_4 to remove photogenerated CO. All thermal reactions with dienes according to eq 1 were carried out with freshly prepared solutions of $Ru(CO)_3(C_2H_4)_2$.

$Ru(CO)_4(\eta^2$-1,4-pentadiene), $Ru(CO)_4(\eta^2$-3-methyl-1,4-pentadiene), $Ru(CO)_4(\eta^2$-1,5-hexadiene), and $Ru(CO)_4(\eta^2$-1,6-heptadiene) were prepared via a modification of the preparation for $Ru(CO)_4(C_2H_4)$. Visible-light ($\lambda > 420$ nm) irradiation of ~0.4 m*M* $Ru_3(CO)_{12}$ in a 3-methylpentane solution containing ~1 M diene at 298 K cleanly yields $Ru(CO)_4(\eta^2$-diene).

IR data for complexes studied are found in Table I. In general we are not able to isolate the $Ru(CO)_n(olefin)_{5-n}$ (n = 4, 3) complexes or obtain clean NMR data, since these complexes are stable only in the presence of excess olefin. A sample of $Ru(CO)_3(\eta^4$-1,5-hexadiene) for ^1H NMR analysis was obtained either by thermal reaction of $Ru(CO)_3(C_2H_4)_2$ with excess 1,5-hexadiene or by near-UV irradiation of $Ru_3(CO)_{12}$ in the presence of excess 1,5-hexadiene in benzene-d_6. In both cases aliquot solutions were withdrawn simultaneously and monitored by IR spectroscopy to ensure the clean formation of $Ru(CO)_3(\eta^4$-1,5-hexadiene). ^1H NMR (C_6D_6): δ 1.52 ($C_{1,6}H_a$, d, 2 H, J = 5 Hz), 1.60 ($C_{1,6}H_b$, d, 2 H, J = 6 Hz), ~1.90 ($C_{3,4}H_{endo}$, m, 2 H), 2.65 ($C_{3,4}H_{exo}$, m, 2 H), 4.39 ($C_{2,5}H$, m, 2 H).

Results and Discussion

(a) Thermal Reaction of $Ru(CO)_3(C_2H_4)_2$ with 1,4-Pentadiene and 3-Methyl-1,4-pentadiene.

Addition of 1,4-pentadiene to a concentration of ~1 M to an alkane/C_2H_4 solution of ~1 mM $Ru(CO)_3(C_2H_4)_2$, at 298 K leads to rapid IR spectral changes that are consistent with the substitution reaction represented by eq 3. The difference IR spectra in Figure 1 show that the three

$$Ru(CO)_3(C_2H_4)_2 + \text{1,4-pentadiene} \xrightarrow{298\ K} Ru(CO)_3(\eta^4\text{-1,4-pentadiene}) + 2C_2H_4 \quad (3)$$

absorption bands in the CO stretching region due to $Ru(CO)_3(C_2H_4)_2$ decrease in intensity immediately upon mixing and two new bands at 2050 and 1966 cm^{-1} increase in intensity. The 2050- and 1966-cm^{-1} bands in the IR spectrum differ from those observed for $Ru(CO)_3(alkene)_2$, $Ru(CO)_3(\eta^4$-1,3-diene), and $HRu(CO)_3(\eta^3$-allyl) (Table I). We assign the bands at 2050 and 1966 cm^{-1} to the complex $Ru(CO)_3(\eta^4$-1,4-pentadiene). The $Ru(CO)_3(\eta^4$-1,4-pentadiene) complex has a third CO stretching band at 1992 cm^{-1}, which is obscured in the difference IR spectra by the band at 1995 cm^{-1} due to $Ru(CO)_3(C_2H_4)_2$.

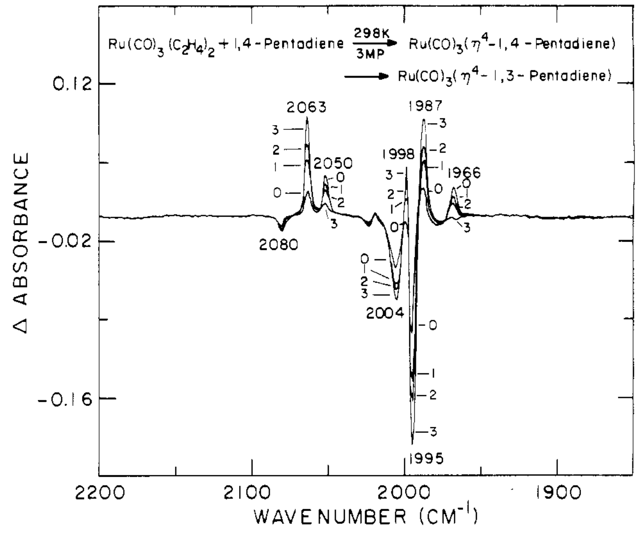


Figure 1. IR difference spectral changes accompanying thermal reaction of ~1 mM $Ru(CO)_3(C_2H_4)_2$ with 1,4-pentadiene in 3-methylpentane solution at 298 K (Δt = 60, 90, 120, 180 s). The positive peaks at 2050 and 1966 cm^{-1} are due to the intermediate $Ru(CO)_3(\eta^4$-1,4-pentadiene). The spectra were taken as the concentration of this intermediate was decreasing with time and isomerizing to $Ru(CO)_3(\eta^4$-1,3-pentadiene). The positive peaks at 2063, 1998, and 1987 cm^{-1} are due to this product.

As reported earlier,[1] $Ru(CO)_3(C_2H_4)_2$ reacts rapidly with L (L = CO, PPh_3, alkene) yielding $Ru(CO)_3(L)_2$. However, there are no bands attributable to $Ru(CO)_3(\eta^2$-1,4-pentadiene$)_2$ in the IR spectrum from the reaction of $Ru(CO)_3(C_2H_4)_2$ and ~1 *M* 1,4-pentadiene. We attribute the lack of formation of $Ru(CO)_3(\eta^2$-1,4-pentadiene$)_2$ to the ability of 1,4-pentadiene to bind preferentially as a chelating ligand. Despite the thermodynamic chelate effect, the diene ligand in an alkane solutions of $Ru(CO)_3(\eta^4$-1,4-pentadiene) is very rapidly replaced by reaction with 0.05 M PPh_3 yielding $Ru(CO)_3(PPh_3)_2$ within 1 min.

As shown in Figure 1, $Ru(CO)_3(\eta^4$-1,4-pentadiene) isomerizes with a half-time of about 2 min at 298 K to give $Ru(CO)_3(\eta^4$-1,3-pentadiene) having bands at 2063, 1998, and 1987 cm^{-1}. The structure of this complex is assigned by comparison of IR and GC-MS data with that from an authentic sample prepared in-

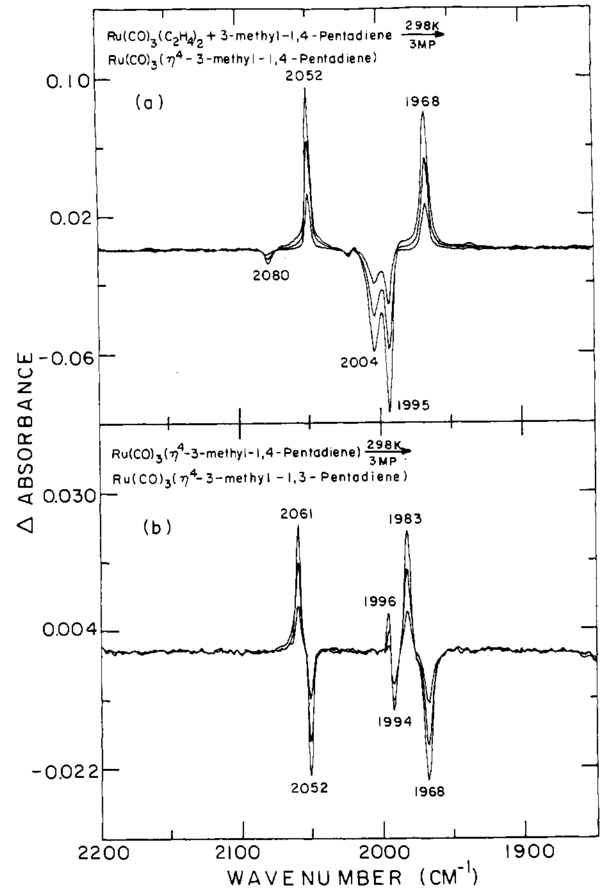
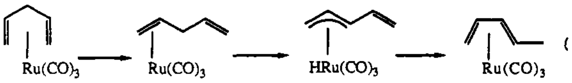


Figure 2. (a) IR difference spectral changes accompanying thermal reaction of $Ru(CO)_3(C_2H_4)_2$ with 3-methyl-1,4-pentadiene in 3-methylpentane solution at 298 K (Δt = 30, 60, 90 s). The positive peaks at 2052 and 1968 cm^{-1} correspond to $Ru(CO)_3(\eta^4$-3-methyl-1,4-pentadiene). (b) IR difference spectral changes accompanying thermal isomerization of $Ru(CO)_3(\eta^4$-3-methyl-1,4-pentadiene) from the reaction in part a in 3-methylpentane solution at 298 K (Δt = 30, 60, 90 min). The positive peaks at 2061, 1996, 1983 cm^{-1} correspond to $Ru(CO)_3(\eta^4$-3-methyl-1,3-pentadiene).

dependently by reaction of $Ru(CO)_3(C_2H_4)_2$ and 1,3-pentadiene. We presume[15] that the isomerization of the 1,4-pentadiene occurs via dechelation of the diene, oxidative addition of an allylic C–H bond yielding a π-allyl hydride complex followed by reductive elimination of a new allylic C–H bond, eq 4. Light-induced loss



(4)

of CO from $Ru(CO)_4(\eta^2$-1,4-pentadiene) can also yield the presumed coordinatively unsaturated η^2-1,4-pentadiene intermediate and ultimately does yield the conjugated diene product (vide infra). Furthermore, low-temperature photochemical experiments with $Ru(CO)_4(\eta^2$-1,4-pentadiene), vide infra, have been used to detect the π-allyl hydride intermediate.

Similar to 1,4-pentadiene, addition of ~1 M 3-methyl-1,4-pentadiene to an alkane/C_2H_4 solution of ~1 mM $Ru(CO)_3(C_2H_4)_2$ at 298 K also results in the rapid decline of IR spectral features for $Ru(CO)_3(C_2H_4)_2$ and growth of new features attributed to $Ru(CO)_3(\eta^4$-3-methyl-1,4-pentadiene) (Figure 2a). The three CO stretching bands at 2052, 1994, and 1968 cm^{-1} for $Ru(CO)_3(\eta^4$-3-methyl-1,4-pentadiene) are remarkably similar to those for $Ru(CO)_3(\eta^4$-1,4-pentadiene) (Table I). $Ru(CO)_3(\eta^4$-3-methyl-1,4-pentadiene) isomerizes with a half-time of >3 h at 298 K to $Ru(CO)_3(\eta^4$-3-methyl-1,3-pentadiene) (Figure 2b). The slow isomerization of $Ru(CO)_3(\eta^4$-3-methyl-1,4-pentadiene)

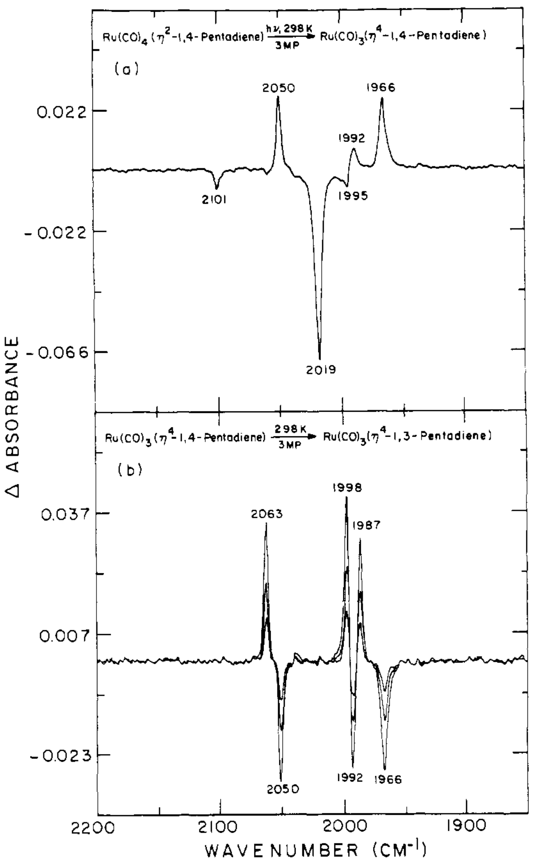


Figure 3. (a) IR difference spectral changes measured ~1 min after a 50-μs flash photolysis of $Ru(CO)_4(\eta^2$-1,4-pentadiene) in 3-methylpentane solution containing 1,4-pentadiene at 298 K. The positive peaks at 2050, 1992, and 1966 cm^{-1} correspond to $Ru(CO)_3(\eta^4$-1,4-pentadiene). (b) IR difference spectral changes accompanying thermal isomerization of $Ru(CO)_3(\eta^4$-1,4-pentadiene) from the reaction in part a in 3-methylpentane solution at 298 K (Δt = 30, 60, 120 s). The positive peaks at 2063, 1998, and 1987 cm^{-1} correspond to $Ru(CO)_3(\eta^4$-1,3-pentadiene).

compared to $Ru(CO)_3(\eta^4$-1,4-pentadiene) is probably not only due to the replacement of one doubly allylic hydrogen by a methyl group but is also due to steric hindrance associated with the methyl substituent in formation of a π-allyl hydride intermediate.

(b) Photoreaction of $Ru(CO)_4(\eta^2$-1,4-pentadiene) and $Ru(CO)_4(\eta^2$-3-methyl-1,4-pentadiene) at 298 K. The complex $Ru(CO)_4(\eta^2$-1,4-pentadiene) can be made via visible-light ($\lambda > 420$ nm) irradiation of an alkane solution of $Ru_3(CO)_{12}$ at 298 K, eq 2. The complex $Ru(CO)_4(\eta^2$-1,4-pentadiene) is, however, only stable in the presence of an excess of 1,4-pentadiene (1 M is typically used). The selective irradiation of $Ru_3(CO)_{12}$ is a general and efficient way to synthesize $Ru(CO)_4(\eta^2$-olefin) (olefin = C_2H_4, C_3H_6, C_5H_{10}, 1,3-pentadiene, 1,4-pentadiene, 3-methyl-1,4-pentadiene, 1,5-hexadiene, 1,6-heptadiene) (Table I). Owing to thermodynamic considerations, it is logical to conclude that all of the η^2-diene complexes involve binding to Ru via the terminal double bond,[16] but this has not been unambiguously established.

Xenon flash (~50 μs) photolysis of ~1 mM $Ru(CO)_4(\eta^2$-1,4-pentadiene) in a 3-methylpentane solution at 298 K containing ~1 M 1,4-pentadiene yields $Ru(CO)_3(\eta^4$-1,4-pentadiene) via light-induced loss of CO, eq 5 (Figure 3a). The difference IR

$$Ru(CO)_4(\eta^2\text{-1,4-pentadiene}) \xrightarrow[\text{1,4-pentadiene}]{h\nu,\ 298\ K} Ru(CO)_3(\eta^4\text{-1,4-pentadiene}) + CO \quad (5)$$

spectrum of $Ru(CO)_3(\eta^4$-1,4-pentadiene) associated with this reaction shows the same bands for product as observed in the

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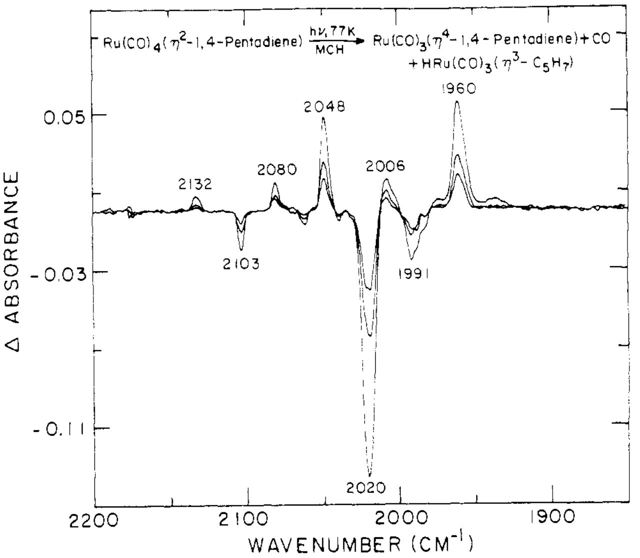


Figure 4. IR difference spectral changes due to near-UV irradiation of ~1 mM Ru(CO)$_4$(η^2-1,4-pentadiene) in a methylcyclohexane matrix containing ~1 M 1,4-pentadiene at 77 K. The positive peaks at 2048 and 1960 cm^{-1} are due to Ru(CO)$_3$(η^4-1,4-pentadiene), the peaks at 2080 and 2006 cm^{-1} are due to HRu(CO)$_3$(η^3-C$_5$H$_7$), and the peak at 2132 cm^{-1} is due to free CO.

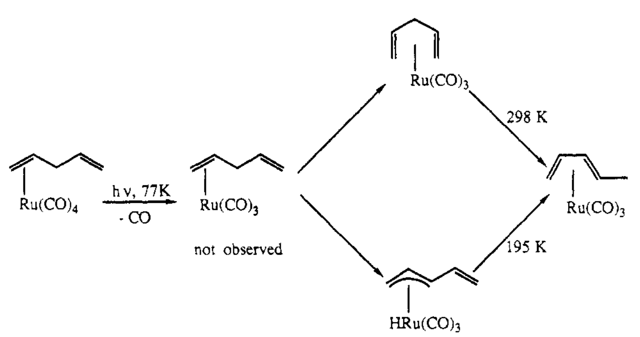
thermal reaction of Ru(CO)$_3$(C$_2$H$_4$)$_2$ with 1,4-pentadiene (Figure 1), except that the peak at 1992 cm^{-1} for Ru(CO)$_3$(η^4-1,4-pentadiene) is less obscured by the peak at 1994 cm^{-1} of Ru(CO)$_4$(η^2-1,4-pentadiene). The complex Ru(CO)$_3$(η^4-1,4-pentadiene) isomerizes to Ru(CO)$_3$(η^4-1,3-pentadiene) as discussed above with a half-time of ~2 min at 298 K. Figure 3b shows IR spectral data for the isomerization reaction. The data reveal that both the Ru(CO)$_3$(η^4-1,4-pentadiene) and Ru(CO)$_3$(η^4-1,3-pentadiene) complexes clearly have three CO absorption bands.

Xenon flash photolysis of ~1 mM Ru(CO)$_4$(η^2-3-methyl-1,4-pentadiene) in a 3-methylpentane solution at 298 K containing ~1 M 3-methyl-1,4-pentadiene yields Ru(CO)$_3$(η^4-3-methyl-1,4-pentadiene), which shows the same bands as observed in the thermal reaction of Ru(CO)$_3$(C$_2$H$_4$)$_2$ with 3-methyl-1,4-pentadiene. The follow-up thermal isomerization of Ru(CO)$_3$(η^4-3-methyl-1,4-pentadiene) occurs with a half-time of >3 h, as found from studies beginning with Ru(CO)$_3$(C$_2$H$_4$)$_2$.

(c) Photoreaction of Ru(CO)$_4$(η^2-1,4-pentadiene) in a Methylcyclohexane Glass. In order to observe the unstable intermediates associated with the chemistry in eq 4 and 5, we studied the photochemistry of Ru(CO)$_4$(η^2-1,4-pentadiene) in a methylcyclohexane matrix at 77 K. When ~1 mM Ru(CO)$_4$(η^2-1,4-pentadiene) is irradiated in a rigid 1,4-pentadiene-containing (~1 M) glass, bands characteristic of free CO (2132 cm^{-1}) and Ru(CO)$_3$(η^4-1,4-pentadiene) (2048, 1960 cm^{-1}) are observed in the IR spectra (Figure 4). The rigid glass precludes diffusion of the presumed Ru(CO)$_3$(η^2-1,4-pentadiene) intermediate, thus ruling out polynuclear species as photoproducts. The rigid glass will, however, allow association of the free double bond of the η^2-1,4-pentadiene ligand with the vacant coordination site resulting from loss of CO to give Ru(CO)$_3$(η^4-1,4-pentadiene). We have not observed any bands in the IR spectra at 77 K assignable to Ru(CO)$_3$(η^2-1,4-pentadiene), which we presume to be the primary photoproduct. Ru(CO)$_3$(η^2-1,4-pentadiene) might be able to be observed at temperatures lower than 77 K, since Ru(CO)$_3$(C$_2$H$_4$) has been observed upon photolysis of Ru(CO)$_4$(C$_2$H$_4$) in a 3-methylpentane glass at 55 K[1] (Table I). Also, we do not find Ru(CO)$_3$(η^2-1,4-pentadiene)$_2$ as a product, which might be expected owing to the presence of excess 1,4-pentadiene. However, if the concentration of 1,4-pentadiene is increased from 1 to 4 M, we do observe Ru(CO)$_3$(η^2-1,4-pentadiene)$_2$ as a product (~20%) at 77 K. This assignment is based on IR spectral similarity to Ru(CO)$_3$(C$_2$H$_4$)$_2$ and other bis(olefin) complexes (Table I).

There are important bands at 2080 and 2006 cm^{-1} in the IR spectra recorded after photolysis of Ru(CO)$_4$(η^2-1,4-pentadiene) at 77 K due to a second product (~25%) (Figure 4). On the basis of the similarity of the frequencies and relative intensities of these bands to those for the known complexes HRu(CO)$_3$(η^3-allyl) (allyl = C$_3$H$_5$, C$_5$H$_9$), we assign the bands at 2080 and 2006 cm^{-1} to the allyl hydride complex HRu(CO)$_3$(η^3-C$_5$H$_7$) (Table I). Evidently, association of the free olefin and oxidative addition of the allylic C–H bonds of the η^2-1,4-pentadiene ligand in the presumed primary photoproduct, Ru(CO)$_3$(η^2-pentadiene), are competitive processes in the photolysis of Ru(CO)$_4$(η^2-1,4-pentadiene) at 77 K.

Scheme I. Photochemistry of Ru(CO)$_4$(η^2-1,4-pentadiene)



Warming the matrix containing the photogenerated HRu(CO)$_3$(η^3-C$_5$H$_7$) to 195 K results in the loss of the bands due to HRu(CO)$_3$(η^3-C$_5$H$_7$) and growth in bands for Ru(CO)$_3$(η^4-1,3-pentadiene). Bands due to photogenerated Ru(CO)$_3$(η^4-1,4-pentadiene) survive the warmup process to 195 K. Further warmup to 298 K yields quantitative formation of Ru(CO)$_3$(η^4-1,3-pentadiene). This experiment demonstrates that HRu(CO)$_3$(η^3-C$_5$H$_7$) can be an intermediate in the photochemical formation of Ru(CO)$_3$(η^4-1,3-pentadiene) from Ru(CO)$_4$(η^2-1,4-pentadiene) and is chemically competent to be an intermediate in the thermal isomerization of Ru(CO)$_3$(η^4-1,4-pentadiene) to Ru(CO)$_3$(η^4-1,3-pentadiene).

The photochemistry of Ru(CO)$_4$(η^2-1,4-pentadiene) in an alkane matrix at 77 K in the presence of excess 1,4-pentadiene and the thermal reaction of these intermediates when they are allowed to warm are summarized in Scheme I.

(d) Thermal Reaction of Ru(CO)$_3$(C$_2$H$_4$)$_2$ with 1,5-Hexadiene. Addition of 1 M 1,5-hexadiene to an alkane solution of 1 mM Ru(CO)$_3$(C$_2$H$_4$)$_2$ at 298 K results in IR spectral changes consistent with the substitution reaction represented by eq 6. Two new bands

$$\mathrm{Ru(CO)_3(C_2H_4)_2} + \text{1,5-hexadiene} \xrightarrow{298\ \mathrm{K}} \mathrm{Ru(CO)_3}(\eta^4\text{-1,5-hexadiene}) + 2\mathrm{C_2H_4} \quad (6)$$

at 2050 and 1966 cm^{-1} appear in the IR spectra, and the bands due to Ru(CO)$_3$(C$_2$H$_4$)$_2$ decrease in intensity immediately after addition of 1,5-hexadiene to a solution of Ru(CO)$_3$(C$_2$H$_4$)$_2$ (Figure 5). We assign the product in eq 6 to be Ru(CO)$_3$(η^4-1,5-hexadiene) based on its IR and ^{1}H NMR spectra. The IR spectrum for the complex is remarkably similar to the IR spectra of Ru(CO)$_3$(η^4-1,4-pentadiene) and Ru(CO)$_3$(η^4-3-methyl-1,4-pentadiene) (Table I). The coordinated 1,5-hexadiene in Ru(CO)$_3$(η^4-1,5-hexadiene) can also be replaced within 1 min at 298 K by reaction with 0.05 M PPh$_3$, yielding Ru(CO)$_3$(PPh$_3$)$_2$.

In contrast to Ru(CO)$_3$(η^4-1,4-pentadiene) or Ru(CO)$_3$(η^4-3-methyl-1,4-pentadiene), the complex Ru(CO)$_3$(η^4-1,5-hexadiene) is stable at 298 K in alkane solution under an inert atmosphere for hours. We attribute the rapid rate of isomerization of Ru(CO)$_3$(η^4-1,4-pentadiene) to Ru(CO)$_3$(η^4-1,3-pentadiene) to the presence of two doubly allylic hydrogens in 1,4-pentadiene. Due to the steric effect of the methyl substituent on 3-methyl-1,4-pentadiene on the isomerization process, Ru(CO)$_3$(η^4-3-methyl-1,4-pentadiene), with only one doubly allylic hydrogen, shows a much slower rate of isomerization to Ru(CO)$_3$(η^4-3-methyl-1,3-pentadiene). Despite the substitution lability of Ru(CO)$_3$(η^4-1,5-hexadiene), it is surprisingly inert to isomerization. ^{1}H NMR spectroscopy indicates that Ru(CO)$_3$(η^4-1,5-hexadiene) is the predominant product upon mixing Ru(CO)$_3$(C$_2$H$_4$)$_2$ with 1,5-

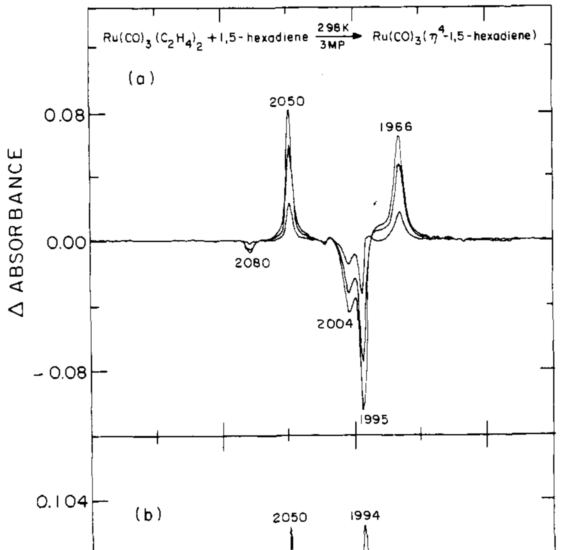


Figure 5. (a) IR difference spectral changes accompanying thermal reaction of $Ru(CO)_3(C_2H_4)_2$ with 1,5-hexadiene in 3-methylpentane solution at 298 K (Δt = 30, 60, 90 s). The positive peaks at 2050 and 1966 cm^{-1} correspond to $Ru(CO)_3(\eta^4$-1,5-hexadiene). (b) IR spectrum for $Ru(CO)_3(\eta^4$-1,5-hexadiene) after thermal reaction described in part a was completed. The peak at 2019 cm^{-1} is due to a trace amount of $Ru(CO)_4(\eta^2$-1,5-hexadiene).

hexadiene; only small amount of species (< 5%) attributable to the isomerization products were formed within 1 h at room temperature. However, $Ru(CO)_3(C_2H_4)_2$ is not very active as an isomerization catalyst toward 1-pentene either, though the bis(1-pentene) complex is very substitution labile.[1]

(e) Photoreaction of $Ru(CO)_4(\eta^2$-1,5-hexadiene) at 298 K. Flash photolysis of 1 mM $Ru(CO)_4(\eta^2$-1,5-hexadiene) in a 3-methylpentane solution at 298 K containing 1 M 1,5-hexadiene leads to IR spectral changes that are consistent with the reaction represented by eq 7. The difference IR spectrum shows that the

$$Ru(CO)_4(\eta^2\text{-1,5-hexadiene}) \xrightarrow[\text{1,5-hexadiene}]{h\nu,\ 298\ K} Ru(CO)_3(\eta^4\text{-1,5-hexadiene}) + CO \quad (7)$$

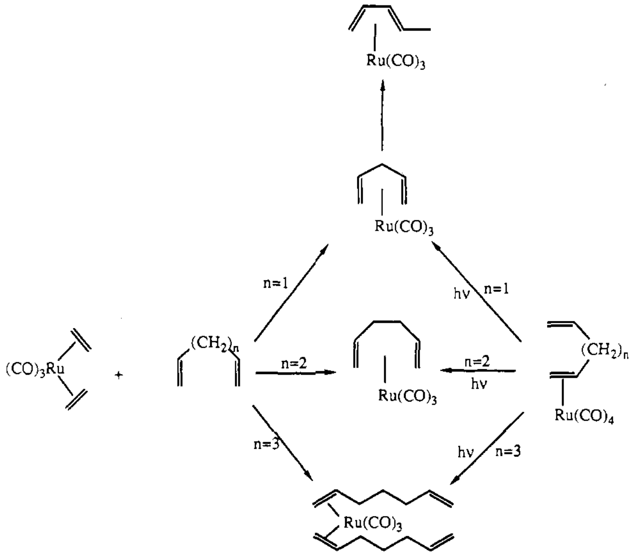
three bands for $Ru(CO)_4(\eta^2$-1,5-hexadiene) decrease and two new bands at 2050 and 1966 cm^{-1} increase in intensity. The positions of these bands are the same as those observed in the thermal reaction of $Ru(CO)_3(C_2H_4)_2$ with 1,5-hexadiene.

(f) Thermal Reaction of $Ru(CO)_3(C_2H_4)_2$ with 1,6-Heptadiene. Addition of ~1 M 1,6-heptadiene to an alkane solution of ~1 mM $Ru(CO)_3(C_2H_4)_2$ at 298 K results in IR spectral changes consistent with the substitution reaction represented by eq 8. The

$$Ru(CO)_3(C_2H_4)_2 + \text{1,6-heptadiene} \xrightarrow{298\ K} Ru(CO)_3(\eta^2\text{-1,6-heptadiene})_2 + 2C_2H_4 \quad (8)$$

difference IR spectrum shows that the three CO absorption bands due to $Ru(CO)_3(C_2H_4)_2$ decrease in intensity immediately upon mixing and new bands at 2074 and 1986 cm^{-1} attributed to $Ru(CO)_3(\eta^2$-1,6-heptadiene)$_2$ increase in intensity. This assignment of the product is based on the spectral similarity to the bis(ethylene) complex and other bis(olefin) complexes. The shift to lower frequencies is consistent with the substitution of C_2H_4 by 1,6-heptadiene (Table I). Interestingly, the product obtained from the reaction of $Ru(CO)_3(C_2H_4)_2$ and 1,6-heptadiene is not $Ru(CO)_3(\eta^4$-1,6-heptadiene) but $Ru(CO)_3(\eta^2$-1,6-heptadiene)$_2$. The reactivity difference between 1,6-heptadiene and the 1,4- and 1,5-dienes with $Ru(CO)_3(C_2H_4)_2$ is presumably due to the fact that the two double bonds of 1,6-heptadiene are too far apart for a cooperative chelate effect. $Ru(CO)_3(\eta^2$-1,6-heptadiene)$_2$ reacts with 0.05 M PPh_3 at 298 K yielding $Ru(CO)_3(PPh_3)_2$ within 1 min, demonstrating that it too is a very labile complex.

Scheme II. Photochemistry of $Ru(CO)_4(\eta^2$-diene) (Diene = 1,4-Pentadiene, 1,5-Hexadiene, 1,6-Heptadiene) and Thermal Reaction of $Ru(CO)_3(C_2H_4)_2$ and Dienes in an Alkane Solution at 298 K



(g) Photochemistry of $Ru(CO)_4(\eta^2$-1,6-heptadiene) at 298 K. Xenon flash photolysis of $Ru(CO)_4(\eta^2$-1,6-heptadiene) in an alkane solution containing 1 M 1,6-heptadiene results in the formation of $Ru(CO)_3(\eta^2$-1,6-heptadiene)$_2$, eq 9. The IR spectrum of

$$Ru(CO)_4(\eta^2\text{-1,6-heptadiene}) \xrightarrow[\text{1,6-heptadiene}]{h\nu,\ 298\ K} Ru(CO)_3(\eta^2\text{-1,6-heptadiene})_2 + CO \quad (9)$$

$Ru(CO)_3(\eta^2$-1,6-heptadiene)$_2$ produced in this reaction shows the same bands as observed in the thermal reaction of $Ru(CO)_3(C_2H_4)_2$ with 1,6-heptadiene.

Conclusions

As summarized in Scheme II, the photoreaction of $Ru(CO)_4(\eta^2$-diene) and the thermal reaction of $Ru(CO)_3(C_2H_4)_2$ with the diene give the same products. The products can be either $Ru(CO)_3(\eta^4$-diene) or $Ru(CO)_3(\eta^2$-diene)$_2$, depending on the number of saturated carbons between terminal double bonds. The chelation effect is significant for 1,4-pentadiene, 3-methyl-1,4-pentadiene, and 1,5-hexadiene, but 1,6-heptadiene does not form a chelate complex.

The presence of two doubly allylic hydrogens in $Ru(CO)_3(\eta^4$-1,4-pentadiene) permits it to rapidly isomerize to $Ru(CO)_3(\eta^4$-1,3-pentadiene) at 298 K. Replacing one of the two doubly-allylic hydrogens by a methyl group significantly slows down the rate of isomerization at 298 K of $Ru(CO)_3(\eta^4$-3-methyl-1,4-pentadiene) to $Ru(CO)_3(\eta^4$-3-methyl-1,3-pentadiene). In contrast, $Ru(CO)_3(\eta^4$-1,5-hexadiene) is stable for several hours under the same conditions. We are not able to observe $Ru(CO)_3(\eta^2$-1,4-pentadiene) on irradiation of $Ru(CO)_4(\eta^2$-1,4-pentadiene) at 77 K. The significant products at 77 K are $Ru(CO)_3(\eta^4$-1,4-pentadiene) and $HRu(CO)_3(\eta^3$-$C_5H_7)$, which isomerizes to $Ru(CO)_3(\eta^4$-1,3-pentadiene) above 195 K. Thus, low-temperature photochemistry of $Ru(CO)_4(\eta^2$-1,4-pentadiene) provides evidence that $HRu(CO)_3(\eta^3$-$C_5H_7)$ can be an intermediate in the isomerization of $Ru(CO)_3(\eta^4$-1,4-pentadiene) to $Ru(CO)_3(\eta^4$-1,3-pentadiene).

Inorg. Chem. **1988**, *27*, 3044–3051

We have demonstrated that $Ru(CO)_3(C_2H_4)_2$ not only is a catalyst for alkene isomerization[1] but also serves as a "$Ru(CO)_3$" transfer reagent, permitting the synthesis of novel, thermally labile ruthenium complexes of acyclic nonconjugated dienes.

Acknowledgment. We thank the National Science Foundation and the Office of Naval Research for support of this work.

Registry No. $Ru_3(CO)_{12}$, 15243-33-1; $Ru(CO)_3(PPh_3)_2$, 14741-36-7; $Ru(CO)_3(C_2H_4)$, 115512-39-5; $Ru(CO)_4(C_2H_4)$, 52621-15-5; $Ru(CO)_4(C_3H_6)$, 106520-68-7; $Ru(CO)_4(C_5H_{10})$, 67606-17-1; $Ru(CO)_4(\eta^2$-1,4-pentadiene), 115512-40-8; $Ru(CO)_4(\eta^2$-3-Me-1,4-$C_5H_7)$, 115512-41-9; $Ru(CO)_4(\eta^2$-1,5-hexadiene), 115512-42-0; $Ru(CO)_4(\eta^2$-1,6-heptadiene), 115512-43-1; $Ru(CO)_3(C_2H_4)_2$, 106520-58-5; $Ru(CO)_3(C_3H_6)_2$, 106520-70-1; $Ru(CO)_3(C_5H_{10})_2$, 106520-67-6; $Ru(CO)_3(\eta^2$-1,4-pentadiene$)_2$, 115512-44-2; $Ru(CO)_3(\eta^2$-1,6-heptadiene$)_2$, 115512-45-3; $Ru(CO)_3(\eta^4$-1,4-pentadiene), 115512-46-4; $Ru(CO)_3(\eta^4$-3-Me-1,4-$C_5H_7)$, 115512-47-5; $Ru(CO)_3(\eta^4$-1,5-hexadiene, 115512-48-6; $Ru(CO)_3(\eta^4$-1,3-pentadiene), 106621-53-8; $Ru(CO)_3(\eta^4$-3-Me-1,3-$C_5H_7)$, 115512-49-7; $Ru(CO)_3(\eta^4$-1,3-butadiene), 62883-45-8; $HRu(CO)_3(\eta^3$-$C_3H_5)$, 106520-69-8; $HRu(CO)_3(\eta^3$-$C_5H_9)$, 106520-72-3; $HRu(CO)_3(\eta^3$-$C_5H_7)$, 115512-50-0.

Supplementary Material Available: Two figures showing IR spectral changes for $Ru(CO)_4(\eta^2$-1,5-hexadiene) flash photolysis in the presence of 1,5-hexadiene forming $Ru(CO)_3(\eta^4$-1,5-hexadiene) and for thermal reaction of $Ru(CO)_3(C_2H_4)_2$ with 1,6-heptadiene forming $Ru(CO)_3(\eta^2$-1,6-heptadiene$)_2$ (2 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
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Synthesis, Characterization, and Oxygen Atom Transfer Reactions of $\{HB(Me_2C_3N_2H)_3\}MoO\{S_2P(OR)_2\}$ and $\{HB(Me_2C_3N_2H)_3\}MoO_2\{\eta^1\text{-}S_2P(OEt)_2\}$

Sue A. Roberts, Charles G. Young, W. E. Cleland, Jr., Richard B. Ortega, and John H. Enemark*

Received August 26, 1987

The compounds $\{HB(Me_2pz)_3\}MoO\{S_2P(OEt)_2\}$ (**1a**) and $\{HB(Me_2pz)_3\}MoO_2\{S_2P(OEt)_2\}$ (**2**) containing bidentate and monodentate $S_2P(OEt)_2^-$ ligands, respectively, have been prepared by the reaction of $Mo_2O_3\{S_2P(OEt)_2\}_4$ with $K\{HB(Me_2pz)_3\}$. $\{HB(Me_2pz)_3\}MoO\{S_2P(OEt)_2\}$ and its analogue $\{HB(Me_2pz)_3\}MoO\{S_2P(OMe)_2\}$ have also been prepared in higher yield by the reaction of $Mo_2O_3\{S_2P(OEt)_2\}_4$ with Ph_3P followed by reaction with $K\{HB(Me_2pz)_3\}$. Both **1a** and **2** have been structurally characterized by X-ray crystallography. The blue Mo(IV) compound **1a** crystallizes in the monoclinic space group $P2_1/c$ with $a = 17.987$ (3) Å, $b = 8.219$ (3) Å, $c = 18.681$ (7) Å, $\beta = 104.88$ (2)°, and $Z = 4$. The molybdenum atom is six-coordinate and facially coordinated by the tridentate $HB(Me_2pz)_3^-$ ligand, by one terminal oxo ligand (Mo=O = 1.644 (6) Å) and by the bidentate $S_2P(OEt)_2^-$ ligand. The gold-colored Mo(VI) complex **2** crystallizes as the toluene hemisolvate in the triclinic space group $P\bar{1}$ with $a = 8.421$ (1) Å, $b = 12.654$ (6) Å, $c = 15.240$ (5) Å, $\alpha = 87.77$ (3)°, $\beta = 81.36$ (2)°, $\gamma = 74.37$ (3)°, and $Z = 2$. The molybdenum atom is six-coordinate with a tridentate $HB(Me_2pz)_3^-$ ligand, two terminal oxo ligands (Mo=O = 1.690 (2) and 1.697 (2) Å), and a monodentate $S_2P(OEt)_2^-$ ligand. The $S_2P(OEt)_2^-$ ligand adopts an extended geometry, and the uncoordinated sulfur atom is 5.42 Å from the molybdenum atom. Compound **1a** reduces Me_2SO to Me_2S. The kinetic data can be fit to a second-order rate law with $k = 5.46$ (6) $\times 10^{-5}$ (M s$)^{-1}$ in toluene at 40 °C. Activation parameters determined from plots of ln (k/T) vs $1/T$ are $\Delta H^* = 15.3$ (2) kcal mol^{-1} and $\Delta S^* = -29$ (2) cal (mol K$)^{-1}$. The large negative entropy of activation indicates that an associative mechanism is operative. Compound **2** oxidizes Ph_3P to Ph_3PO. Again, a second-order rate law is followed; $k = 3.4$ (1) $\times 10^{-3}$ (M s$)^{-1}$ in toluene at 25 °C. Both complexes catalyze the oxidation of Ph_3P by Me_2SO.

Introduction

Considerable recent research has been directed toward the preparation of mononuclear high-valent oxomolybdenum complexes as structural and reactivity models of the molybdenum site in oxo-type molybdoenzymes.[1] These enzymes catalyze net oxygen atom transfer reactions, as typified by the oxidation of sulfite to sulfate (sulfite oxidase) or the oxidation of xanthine to uric acid (xanthine oxidase).[2] Recently, Hille and Sprecher[3] have shown that the oxygen atom added to xanthine by xanthine oxidase arises from the molybdenum complex exclusively and not from a solvent molecule. Several oxomolybdenum(IV) and oxomolybdenum(VI) complexes containing sulfur-donor ligands are known to undergo oxygen atom transfer reactions.[4] The well-known complex $MoO_2(S_2CNEt_2)_2$ undergoes facile oxygen atom transfer reactions[5] but is unsuitable as a model system for oxo-type molybdoenzymes because a stable oxo-bridged dimer readily forms in solution.[6] In general, comproportionation of molybdenum(IV) and molybdenum(VI) complexes to form stable dinuclear complexes, a common reaction in oxomolybdenum chemistry, must be inhibited to achieve a catalytic cycle.

Berg and Holm[7] have synthesized a five-coordinate dioxomolybdenum(VI) complex containing the 2,6-bis-(2,2-diphenyl-2-mercaptoethyl)pyridine ligand (LNS_2) in which phenyl rings adjacent to the ligating sulfur atoms provide steric hindrance and prevent dimerization upon reduction. The dioxomolybdenum(VI) complex of LNS_2 transfers an oxygen atom to triphenylphosphine (eq 1) to generate an oxo–Mo(IV) complex, which can in turn be reoxidized by an oxygen atom abstraction reaction with Me_2SO (eq 2). Coupling of reactions 1 and 2 results in the catalytic

$$(LNS_2)MoO_2 + Ph_3P \rightarrow (LNS_2)MoO + Ph_3PO \qquad (1)$$

$$(LNS_2)MoO + Me_2SO \rightarrow (LNS_2)MoO_2 + Me_2S \qquad (2)$$

transfer of an oxygen atom from Me_2SO to Ph_3P, a reaction that does not proceed in the absence of a catalyst. These complexes and others[8] that have been reported to catalyze this reaction cycle

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