Photoinduced rearrangements of ring-coupled bis(cyclopentadienylrutheniumdicarbonyl) compounds of the form $Ru_2(CO)_4(\eta^5,\eta^5-C_5H_4LC_5H_4)$ $(L = CH_2-, (CH_3)_2C-,$ C_2H_4- and $(CH_3)_2Si-)$ The molecular structure of $[Ru(CO)_2][Ru(CO)_2Cl](\eta^5,\eta^5:\eta^1-C_5H_4CH_2C_5H_3)$ [1]

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Abstract

Compounds of the general form $Ru_2(CO)_4(\eta^5,\eta^5-C_5H_4LC_5H_4)$, where $L = CH_2-$, $(CH_3)_2C-$, C_2H_4- and $(CH_3)_2Si$ -, have been found to undergo photolysis in deuterobenzene or deuterotoluene to give 'twisted' ruthenium hydride complexes of the form $[Ru(CO)_2][Ru(CO)_2H](\eta^5,\eta^5:\eta^1-C_5H_4LC_5H_3)$. Reaction of these hydrides with chlorocarbons resulted in the formation of the corresponding chlorides which could be isolated and characterized by IR, ^1H and ^{13}C NMR, mass spectrometry, and elemental analysis. In the particular case of $Ru_2(CO)_4[\eta^5,\eta^5-C_5H_4(CH_3)_2SiC_5H_4]$ a secondary photochemical reaction occurs with formation of $[Ru(CO)_2]_2(\mu-\eta^5:\eta^1-C_5H_4)[\mu-(CH_3)_2Si-(\eta^5-C_5H_4)]$ in which Ru–Ru and Cp–Si bonds have been broken and new Ru–Cp and Ru–Si bonds formed. The molecular structure of $[Ru(CO)_2][Ru(CO)_2Cl](\eta^5,\eta^5:\eta^1-C_5H_4CH_2C_5H_3)$ was determined by X-ray crystallography: monoclinic, Cc, $a = 27.636(5)$ Å, $b = 9.058(2)$ Å, $c = 14.545(5)$ Å, $\beta = 120.85(3)°$, $V = 3126(2)$ Å^3, $Z = 8$, $R(F) = 2.29\%$.

Keywords: Ruthenium; Silicon; Cyclopentadienyls; Photochemistry; Metal carbonyl

1. Introduction

Photolysis of $Ru_2(CO)_4(\eta^5-C_5H_5)_2$, **I**, in solution is known to proceed by both radical and carbonyl loss mechanisms. Photolysis of **I** in the presence of CCl_4 or IC_5H_{11} yields $Ru(CO)_2X(\eta^5-C_5H_5)$, where $X = Cl$ and I respectively [1]. Eisenstadt et al. [2], have adapted this reaction to a high yield synthesis of $Ru(CO)_2X(\eta^5-C_5H_5)$, where $X = Cl$ and Br, by photolysis of **I** in CX_4. Photolyses in low temperature matrices have demonstrated that carbonyl loss results in the formation of linear $Ru_2(\mu-CO)_3(\eta^5-C_5H_5)_2$ [3]. The analogous triply carbonyl-bridged iron compound has been ob-

served in solution and in various low temperature matrices [4]. Wrighton and coworkers [5] have reported the molecular structure of $Fe_2(\mu-CO)_3[\eta^5-C_5(CH_3)_5]_2$. Knox and coworkers [6] have reported that extended photolysis of **I** in solution yields a tetraruthenium complex, **II**.

We have reported the synthesis of ring-coupled derivatives of **I** by reaction of $Tl_2(C_5H_4LC_5H_4)$ with $[Cl_2Ru(CO)_3]_2$ to give $Ru_2(CO)_4(\eta^5,\eta^5-C_5H_4LC_5H_4)$, where $L = CH_2$ [7a], **III**, $(CH_3)_2C-$ [7b], **IV**, C_2H_4- [7b], **V**, and $(CH_3)_2Si-$ [7b], **VI**. Knox et al. [8] reported an alternate synthesis of **III** by reaction of the neutral bis(cyclopentadiene)methane ligand with $Ru_3(CO)_{12}$. Photolysis of **III** in frozen gas matrices (Ar and CH_4) leads to the formation of an asymmetric carbonyl-loss product, $Ru_2(CO)_3(\eta^5,\eta^5-C_5H_4CH_2C_5-H_4)$, in which all three carbonyl groups are terminal [3].

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[1] In memory of Professor Alan Campbell Ling, 1940–1995. Mentor and friend.

Knox et al. [8] have photolyzed III in the presence of Ph$_2$C$_2$ and isolated Ru$_2$(CO)$_2$(μ-CO)(μ-σ:σ'-Ph$_2$C$_2$)(η^5,η^5-C$_5$H$_4$CH$_2$C$_5$H$_4$). In the course of our own studies of the photolysis of III with Ph$_2$C$_2$ we consistently observed an additional trace orange product during chromatographic workup of the reaction mixture. Subsequent analysis of this product established that it did not contain a Ph$_2$C$_2$ moiety and prompted us to examine the solution photolysis of III–VI in the absence of potential ligands. This paper describes the results of these studies into the photoinduced structural reorganization of ring-coupled ruthenium compounds. A discussion of the detailed photochemistry and possible mechanism of this reaction will be reported elsewhere [9].

2. Results

The syntheses of Ru$_2$(CO)$_4$(η^5,η^5-C$_5$H$_4$LC$_5$H$_4$), where L = CH$_2$-, III, (CH$_3$)$_2$C-, IV, C$_2$H$_4$-, V, and (CH$_3$)$_2$Si-, VI, have recently been described [7]. IR studies of these compounds have established that III [8] and IV [7a] have solution state structures in which all carbonyl groups are terminal, whereas V and VI prefer conformations in which two of the carbonyl groups are bridging. Molecular structures of III and V confirm that these structural preferences continue into the solid state. ^{13}C NMR of III–VI established that rapid averaging of carbonyl groups occurs at room temperature, indicating that transient bridging-carbonyl forms exist in all cases.

Photolysis of III in thoroughly degassed, deuterated benzene or toluene in a micro-photolysis cell (about 1 ml capacity) resulted in the formation of a new species, VII, whose IR spectrum contains bands at 2033, 2014, 1974, and 1963 cm^{-1}. The ^{1}H NMR spectrum of the photoproduct was characterized by a complex, seven proton resonance cyclopentadienyl ring region, an AB quartet for the bridging methylene group, and a ruthenium hydride resonance. Although one major product was produced in these photolyses, additional resonances are observed in all regions, suggesting that there may be several minor products. VII is very air sensitive and
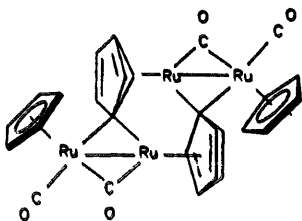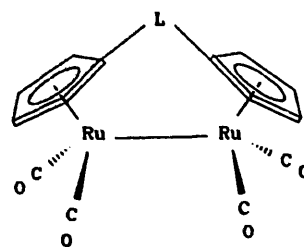
m   L = CH$_2$

IV   L = C(CH$_3$)$_2$

V   L = C$_2$H$_4$

VI   L = Si(CH$_3$)$_2$

reacts to give an insoluble red solid upon brief exposure to air. We have not been successful in obtaining a ^{13}C NMR spectrum of VII.

The red solid formed when VII reacts with air had IR bands at 1992 and 1776 cm^{-1} which are very similar in position to those reported by Knox and coworkers for the tetramer, II; thus we tentatively suggest that the red solid is a ring-coupled analog of II. The ^{1}H NMR spectrum of the red solid was exceedingly complex in the cyclopentadienyl ring region and we have not been able to successfully interpret the spectrum.

Deuterobenzene solutions of III and IV in NMR tubes were rigorously degassed by freeze–pump–thaw techniques. The NMR tubes were placed in a Pyrex water jacket and photolyzed for 15 min using a 350 W high pressure Hg lamp. During this time the solutions changed color from light yellow to dark red. Under these conditions III gave results similar to those from the micro-photolysis vessel, although greater quantities of the secondary ruthenium-hydride products were observed by this method. Microchromatography of the reaction mixtures (after reaction with dichloromethane or CCl$_4$ and removal of solvent) recovered the component that was responsible for the red color and showed it to be identical to the red oxidation product described above. Like III, photolysis of IV gave several products, with the major product having seven proton resonances in the cyclopentadienyl ring region, two resonances in the methyl region and a ruthenium-hydride resonance.

Reaction of VII with dichloromethane or CCl$_4$ yielded an orange crystalline product, VIII. VIII could also be prepared along with the known [Ru(CO)$_2$)Cl]$_2$-(η^5,η^5-C$_5$H$_4$CH$_2$C$_5$H$_4$) when the photolyses of III were carried out in neat CCl$_4$. VIII was the only product when III was photolyzed in 4:1 benzene:dichlo-

II

romethane. The IR spectrum of **VIII** contained four bands in the terminal carbonyl region at 2046, 2028, 1989, and 1975 cm^{-1}. The bands at 2046 and 1989 cm^{-1} are assigned to a CpRu(CO)$_2$Cl moiety, while those at 2028 and 1975 cm^{-1} are typical of CpRu(CO)$_2$R groups.

The ^{1}H NMR spectrum of **VIII** contains a set of seven cyclopentadienyl ring proton resonances, two of which overlap, and an AB quartet for the methylene protons. The ^{13}C NMR spectrum contained resonances for seven protonated ring carbons and three ipso carbons. Four ruthenium carbonyl resonances and a methylene carbon resonance were also observed. COSY allowed assignment of ring proton resonances to the two rings, but full assignment of the resonances was not possible. The spectroscopic evidence strongly suggests a molecular structure in which one of the cyclopentadienyl rings is sigma bonded to a ruthenium atom while still retaining a second, pentahapto bonded ruthenium. This proposed structure was confirmed by X-ray crystallography (vide infra).

Photolysis of **IV** in a 3:1 benzene:chloroform mixture resulted in effectively quantitative conversion of **IV** to a new compound, **IX**, which was found to be identical to a trace side-product from the reaction of Tl$_2$[C$_5$H$_4$(CH$_3$)$_2$CC$_5$H$_4$] with [Cl$_2$Ru(CO)$_3$]$_2$ that we have previously reported. The molecular structure of **IX** was previously determined and established that the compound has a twisted structure. The structure of **IX** will be discussed along with that of **VIII** below.

Photolysis of an NMR sample of **V** in deuterobenzene resulted in the formation of two hydride species (Ru–H at −10.38 and −17.34 ppm). Both the ring and bridge proton regions of this spectrum were complex. An IR spectrum of the sample contained sharp bands at 2032, 2028, and a broad band at 1976 cm^{-1}, similar to
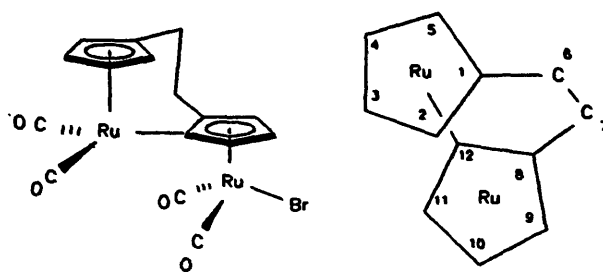

Fig. 1. Proposed conformation and numbering scheme for **X**.

those observed for **VII**. Reaction of a solution containing these hydrides with dichloromethane, or photolysis of **V** in CDCl$_3$ resulted in the formation of a yellow-orange product, **X**. **X** was found to have terminal stretching bands at 2045, 2034, and 1988 cm^{-1}, which are almost identical to those observed for **VIII** and **IX**.

The ^{1}H and ^{13}C NMR spectra of **X** conform to its formulation as a twisted complex with one η^5-Cp ring and one η^5:η^1-Cp ring. The ethylene-bridge resonances form a well resolved set of four doublets of doublets of doublets. COSY, NOESY, and ^{1}H–^{13}C correlation spectra were recorded and allowed a detailed analysis of the solution geometry of the compound. Coupling constants for the doublet of doublet of doublet pattern of the ethylene-bridge hydrogen resonances were obtained. These coupling constants, along with COSY interactions, permitted both the geminal relationships and bridge connectivities relative to the two rings to be established. Applying the Karplus relationship [10], the dihedral angle of the ethylene bridge was found to be about 45°. This angle is in keeping with that obtained using Dreiding stereomodels of the compound. A proposed conformation of the complex and the numbering scheme used in the spectral assignments is presented in Fig. 1.

The bromo analog of **X** has been isolated as a side-product in the reaction of C$_2$H$_4$(C$_5$H$_4$Tl)$_2$/TlBr with [Cl$_2$Ru(CO)$_3$]$_2$ and has been fully characterized [7b].

Photolysis of an NMR sample of **VI** in deuterobenzene gave rise to complex new resonances in the cyclopentadienyl ring region, two new methylsilyl resonances, and a ruthenium-hydride resonance indicative of the formation of a new hydride species analogous to the twisted species described above. Photolysis of **VI** in neat CCl$_4$ yielded a poorly soluble tan solid whose IR and ^{1}H NMR spectrum showed it to be [Ru(CO)$_2$Cl]$_2$-[η^5,η^5-C$_5$H$_4$(CH$_3$)$_2$SiC$_5$H$_4$]. Column chromatography of the CCl$_4$ soluble components of the reaction mixture yielded a trace of a new compound, **XI**. **XI** is the exclusive product when **VI** is photolyzed in a 4:1 benzene:chloroform mixture. IR, ^{1}H and ^{13}C NMR of **XI** are similar to those of the twisted compounds described above and are consistent with classification of
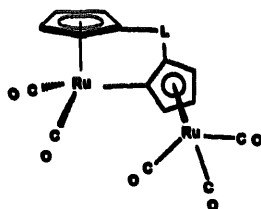
VII	L = CH$_2$, X = H
VIII	L = CH$_2$, X = Cl
IX	L = C(CH$_3$)$_2$, X = Cl
X	L = C$_2$H$_4$, X = Cl
XI	L = Si(CH$_3$)$_2$, X = Cl
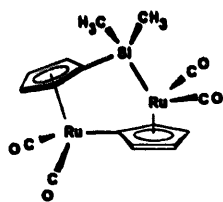
XII

XI as the twist derivative of VI with the formula $[Ru(CO)_2[Ru(CO)_2Cl]\eta^5,\eta^5:\eta^1-C_5H_4(CH_3)_2SiC_5H_3]$. COSY NMR spectra permitted some specific assignments to be made. Accidental overlap of the proton resonances of the hydrogens adjacent to the bridge on the η^5-Cp ring (designated α-η^5-Cp) precluded exact assignment of H-3 and H-4; thus these have been designated simply as β-η^5-Cp. As in most cases, we have not been able to exactly assign protons H-8 and H-10 on ring $\eta^5:\eta^1$-Cp by either COSY or NOESY spectroscopy.

In contrast to the behavior of the carbon-bridged compounds described above, continued irradiation of solutions of VI gave rise to a second, non-hydride species that appeared to grow at the expense of the ruthenium-hydride compound. Column chromatography of the reaction mixture from a microscale photolysis of VI eluted a rapidly moving, very pale yellow compound that gave an almost colorless oil, XII, upon removal of solvent. The IR spectrum of this compound consisted of four bands in the terminal carbonyl region. The simple ^{1}H NMR spectrum consisted of four cyclopentadienyl ring proton resonances and a single methyl-silyl resonance. A GC-MS analysis of the compound showed it to have a parent mass of 500 Da and a fragmentation pattern consistent with sequential loss of four carbonyl groups. The starting material, VI, had a parent mass and fragmentation pattern that were effectively identical to those of XII, with the two compounds differing only in the relative amounts of the carbonyl-loss fragments and in their retention time on the chromatographic column.

These data are consistent with XII being a structural isomer of VI having a unique structure in which one of the cyclopentadienyl-silyl bonds has been broken along with the Ru–Ru bond and the molecule reformed with an Ru–η^1-Cp bond and an Ru–Si bond to give a molecule with the form $[Ru(CO)_2]_2(\mu-\eta^5:\eta^1-C_5H_4)-[\mu-(CH_3)_2Si-(\eta^5-C_5H_4)]$.

In order to clarify the relationship between the intermediate hydride and XII, a sample of VI was photolyzed briefly. After recording a ^{1}H NMR to establish the relative quantities of VI, hydride, and XII, the sample was stored in the dark at 23 °C. Spectra taken of

this sample over a 15 h period demonstrated that the relative ratios of VI and XII did not change significantly, although the hydride slowly disappeared. Heating a similar sample to 65 °C for 5 min resulted in the formation of a fine precipitate. NMR analysis showed significant depletion in the relative quantity of hydride present, but no change in the relative amounts of VI and XII. We cannot distinguish between the possibility that the hydride had thermally rearranged to give both VI and XII, or that traces of air were selectively reacting with the hydride. Photolyses conducted with optical filters, which only passed light shorter than 450 nm and between 400 and 500 nm, yielded both the hydride and XII. Photolysis of VI in neat CCl_4 yielded only XI, but XII was formed along with XI when the photolysis was carried out in toluene with about 10% CCl_4.

The apparent ease of formation of metal-to-ring coupling products in these photochemical reactions of ring-coupled ruthenium compounds prompted us to examine the photolysis of an NMR sample of I in deuterobenzene. A ^{1}H NMR spectrum recorded immediately after photolysis revealed the presence of several hydride products. The cyclopentadienyl ring region contained several resonances and it was not possible to identify any single species with any certainty. We have carried out similar reactions on a number of ring-substituted compounds of the general form $Ru_2(CO)_4(\eta^5-C_5H_4R)_2$, where $R = CH_3$, CH_2Ph, CHO, $COCH_3$, and CO_2CH_3, and found that hydride products are formed in all cases. We have thus far been unsuccessful in cleanly isolating the chloride derivatives of these hydride species; however, we strongly believe that the dominant products have the form $Ru(CO)_2(\eta^5-C_5H_4R)(\mu-\eta^5:\eta^1-C_5H_3R)-Ru(CO)_2H$, although ring-to-ring coupled fulvalene
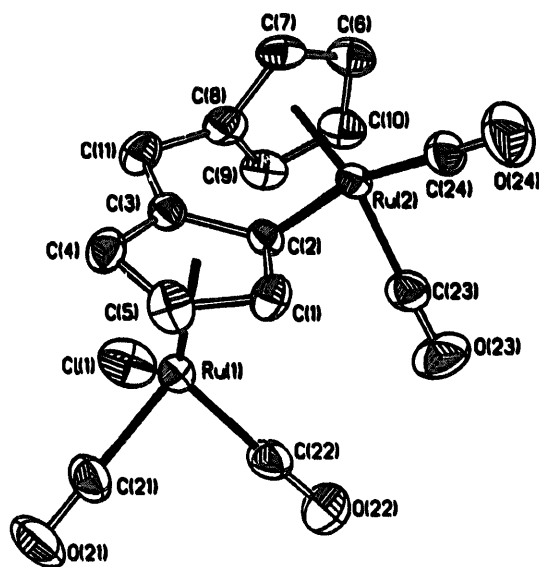
Fig. 2. X-ray crystal structure of VIII.

products such as $[Ru(CO)_2H]_2(\eta^5:\eta^5\text{-}C_5H_4C_5H_4)$ may also be formed. We propose that it is the reaction of these bimetallic hydride species with adventitious oxygen that gave rise to the red tetrameric product, II, reported by Knox and his coworkers.

3. X-ray crystallography

In order to definitively establish the structure of VIII, crystals were grown from dichloromethane–petroleum ether by vapor diffusion in the cold. X-ray crystallographic analyses of these crystals revealed the unique, twisted structures presented in Fig. 2 in which one cyclopentadienyl ring is pentahapto to one ruthenium, while the second ring is monohapto to this ruthenium

Table 1
Crystallographic data for VIII

Crystal parameters	
Formula	$C_{15}H_9ClO_4Ru_2$
Formula weight	490.8
Crystal system	Monoclinic
Space group	Cc
a (Å)	27.636(5)
b (Å)	9.058(2)
c (Å)	14.545(5)
β (deg)	120.8(5)
V (Å^3)	3126(2)
Z	8
Crystal dimensions (mm^3)	0.28×0.29×0.31
Crystal color	orange
D(calc) (g cm^{-3})	2.085
Mo K α (cm^{-1})	20.92
Temperature (K)	293
T(max)/T(min)	1.12
Data collection	
Diffractometer	Nicolet R3m/
Monochromator	graphite
Radiation	Mo K α (λ = 0.71073 Å)
2Θ scan range (deg)	4–52
Data collected (h,k,l)	±33, +9, +17
Reflections collected	3395
Independent reflections	3058
Independent observed reflections	2960 (n = 3)
$F_o \geq n\sigma(F_o)$	
Std./Rfln	3/197
Var. in stds. (%)	< 1
Refinement [a]	
$R(F)$ (%)	2.29
$R(wF)$ (%)	3.15
$\Delta\sigma$(max)	0.04
$\Delta(\rho)$ (e Å^{-3})	0.47
N_o/N_v	7.5
GOF	0.82

[a] Quantity minimized = $\Sigma w\Delta^2$; $R = \Sigma\Delta/\Sigma(F_o)$; $R(w) = \Sigma\Delta w^{1/2}/\Sigma(F_o w^{1/2})$, $\Delta = |(F_o - F_c)|$.

Table 2
Bond lengths and (Å) and angles (deg) for VIII

	Molecule A	Molecule B
Bond distances		
Ru(1)–CNT(1)	1.883(5)	1.892(5)
Ru(1)–Cl(1)	2.419(3)	2.420(3)
Ru(1)–C(21)	1.900(7)	1.865(7)
Ru(1)–C(22)	1.877(8)	1.893(8)
Ru(2)–CNT(2)	1.892(5)	1.895(5)
Ru(2)–C(2)	2.076(5)	2.063(5)
Ru(2)–C(23)	1.888(8)	1.894(10)
Ru(2)–C(24)	1.861(9)	1.858(9)
C(3)–C(11)	1.504(12)	1.498(13)
C(8)–C(11)	1.511(9)	1.506(9)
Ru(1)···Ru(2)	3.9401(4)	3.9472(4)
C(21)–O(21)	1.125(9)	1.145(10)
C(22)–O(22)	1.130(11)	1.136(10)
C(23)–O(23)	1.138(11)	1.115(13)
C(24)–O(24)	1.139(13)	1.138(12)
Bond angles		
CNT(1)–Ru(1)–Cl(1)	121.6(2)	122.3(2)
CNT(1)–Ru(1)–C(21)	127.2(3)	126.8(3)
CNT(1)–Ru(1)–C(22)	125.5(3)	126.7(3)
Cl(1)–Ru(1)–C(21)	91.2(3)	91.9(3)
Cl(1)–Ru(1)–C(22)	90.9(3)	86.3(4)
C(21)–Ru(1)–C(22)	89.9(3)	91.3(3)
CNT(2)–Ru(2)–C(2)	111.5(3)	111.2(3)
CNT(2)–Ru(2)–C(23)	127.7(3)	128.7(3)
CNT(2)–Ru(2)–C(24)	130.5(3)	130.4(3)
C(2)–Ru(2)–C(23)	94.8(3)	92.6(3)
C(2)–Ru(2)–C(24)	90.9(3)	94.1(3)
C(23)–Ru(2)–C(24)	91.3(4)	90.0(4)
Ru(1)–C(21)–O(21)	178.2(6)	176.5(7)
Ru(1)–C(22)–O(22)	176.7(8)	178.1(8)
Ru(2)–C(23)–O(23)	178.8(7)	175.1(9)
Ru(2)–C(24)–O(24)	178.7(6)	177.7(7)
C(3)–C(11)–C(8)	109.0(7)	108.0(7)

and pentahapto to an $Ru(CO)_2Cl$ moiety. With the exception of the methyl groups in the bridge of IX, the molecules of compounds VIII and IX are effectively superimposable. In both cases, the two rings are almost exactly perpendicular to one another. Each of the two geometrically similar ruthenium sites in the two molecules are of the 'three-legged piano stool' type. The interligand angles average about 90°. No bond metric shows evidence of any unusual strain as an accommodation to the formation of the σ (Ru–Cp) bond. Crystallographic data are presented in Table 1 and selected bond lengths and angles are presented in Table 2.

4. Discussion

The studies described above have revealed a previously unobserved, photoinitiated rearrangement of ring-coupled cyclopentadienylrutheniumcarbonyl com-

pounds in which the Ru–Ru bond is broken, and new Ru–σ-Cp and Ru–H bonds are formed. Reaction of the hydride intermediates with various halocarbons give rise to isolable chloride derivatives. No parallel chemistry was observed with the iron analogue of **III**. However, we have recently found similar behavior in ring-coupled heterobimetallic compounds of the general formula $RuM(CO)_5(\eta^5,\eta^5$-C_5H_4-L-$C_5H_4)$, where M = Mo or W and L = CH_2 or $C(CH_3)_2$, as well as the bimetallic molybdenum compound, $M_2(CO)_5(\eta^5,\eta^5$-$C_5H_4CH_2C_5$-$H_4)$. These studies will be reported elsewhere.

Perhaps germane to the mechanism of these rearrangement reactions is the observation that photolyses of the various bridged compounds in neat chlorocarbons such as CCl_4 and $CHCl_3$ give rise to the chloro derivatives, $[Ru(CO)_2Cl]_2(\eta^5,\eta^5$-$C_5H_4LC_5H_4)$, and small quantities of the twist chlorides, whereas the twist compounds are efficiently produced in 4:1 benzene:halocarbon mixtures. Photolysis of **I** in the presence of chlorocarbons to give $Ru(CO)_2Cl(\eta^5$-$C_5H_5)$ is well known and is presumed to proceed by photochemical cleavage of the Ru–Ru bond to give $CpRu(CO)_2$ free radicals which in turn react with the chlorocarbons [1]. We anticipated that ring-coupling would have the effect of keeping the $CpRu(CO)_2$ radicals in close proximity, thus facilitating their thermal back-reaction to reform metal–metal bonds. In neat chlorocarbon solvents, it appears that the photochemically generated radicals can be efficiently intercepted to yield $[Ru(CO)_2Cl]_2[\eta^5,\eta^5$-$C_5H_4LC_5H_4]$ products.

Whether a diradical intermediate is involved in the twist reaction has not yet been determined. Detailed photochemical studies to be reported elsewhere [9] indicate that carbonyl-loss is also observed at the same wavelengths shown to be responsible for the twist reaction, thus the intermediacy of an unsaturated species cannot yet be ruled out.

In the particular case of **VI**, it would appear that the twist hydride itself undergoes a photochemical reaction to yield **XII** in which one $CpRu(CO)_2$ moiety has effectively been rotated relative to its orientation in **VI**. A similar reaction has been reported by Sun et al. [11], in which $Fe_2(CO)_4[\eta^5,\eta^5$-$C_5H_4(CH_3)_2SiC_5H_4]$ is thermally transformed into $[Fe(CO)_2]_2[\mu$-η^5:η^1-$(CH_3)_2SiC_5H_4]$. Perhaps more relevant is the report by Vollhardt and Weidman [12] that the fulvalene derivative, $Ru_2(CO)_4(\eta^5,\eta^5$-$C_5H_4C_5H_4)$, undergoes a photochemical rearrangement to give $[Ru(CO)_2]_2(\mu$-η^5:η^1-$C_5H_4)_2$, which may be restored to its original form by heating. Vollhardt and Weidman tentatively ruled out a radical mechanism for this reaction because this process appeared to be unaffected by the presence of 1 M CCl_4. In the light of the present results, it would appear that the mean lifetimes of a reactive intermediate may be sufficiently long in dilute CCl_4 to allow for radical rearrangement to the observed product.

5. Experimental

5.1. General photolysis procedures

Photolyses were carried out using either an Ace Hanovia medium pressure lamp held in a water-cooled quartz jacket, or a UVP, Inc. 350 W high pressure mercury lamp. Optical filters were purchased from Corion, Inc. NMR samples for photolysis were prepared by either vacuum trap-to-trap transfer of the NMR solvent to an NMR tube containing the ruthenium compound, or by preparation of the solution followed by three freeze–pump–thaw cycles at high vacuum. Microscale photolyses of 10–20 mg of sample were conducted in an Ace 'Micro No-Air' apparatus equipped with a quartz sample tube and a cold finger. Microscale photolysis samples were degassed by three freeze–pump–thaw cycles followed by a nitrogen backflush. NMR tubes were cooled during photolysis by a Pyrex water jacket and microscale photolyses were carried out using a cold finger. IR spectra of air sensitive reaction mixtures were prepared by transfer of sample in a nitrogen flushed syringe to a nitrogen flushed IR cell outfitted with microsepta. The majority of the reactions reported in this work were conducted on either NMR tube or microscales, thus recovered samples were correspondingly small. As a result, mass spectrometry has been the primary tool for chemical analysis in these experiments.

5.2. Photochemical studies of $Ru_2(CO)_4[\eta^5,\eta^5$-C_5H_4-$CH_2C_5H_4]$, III

A solution of **III** in C_6D_6 in an NMR tube was prepared by trap-to-trap transfer, and the solution was photolyzed using an Ace Hanovia lamp without filters. The NMR tube was approximately 5 cm from the lamp. The solution color changed from yellow-orange to red during this period. Spectra recorded after 2 h indicated the formation of a hydride species, **VII**. IR: (C_6D_6)

2033, 2014, 1974, 1963 cm^{-1}. ^{1}H NMR: (C$_6$D$_6$) 4.91 (s, 1H, Cp), 4.70 (s, 2H, Cp), 4.61 (s, 1H, Cp), 4.46 (s, 1H, Cp), 4.48 (s, 2H, Cp), 2.73 and 2.45 (AB quartet, 2H, J_{A-B} = 15.85 Hz), −10.23 (s, 1H, Ru–H).

A microscale sample of III in C$_6$H$_6$ was photolyzed for 2 h using an Ace Hanovia lamp, after which time dichloromethane was injected into the sample and the reaction mixture stirred for an additional hour. After removal of solvent, the residue was taken up in 1:1 petroleum ether:dichloromethane and chromatographed on a 5 mm × 150 mm alumina column. A yellow band was rapidly eluted which was stripped of solvent to give yellow-orange crystals of VIII, m.p. 156–158 °C. IR: (CH$_2$Cl$_2$) 2046, 2029, 1988, 1975 cm^{-1}. ^{1}H NMR: (CDCl$_3$) 5.93 (q, 1H, α-η^5-Cp), 5.59 (m, 2H, β-η^5-Cp), 5.30 (q, 1H, α-η^5-Cp), 5.04 (t, 1H, H8 or H10-η^1:η^5-Cp), 5.01 (q, 1H, H8 or H10-η^1:η^5-Cp), 4.65 (q, 1H, H9-η^1:η^5-Cp), 3.29 and 2.97 (AB quartet, 2H, J_{A-B} = 16.52 Hz, CH$_2$). ^{13}C NMR: (CDCl$_3$) 199.3 (Ru–CO), 198.7 (Ru–CO), 198.2 (Ru–CO), 197.9 (Ru–CO), 144.6 (ipso Cp), 129.4 (ipso Cp), 106.9 (ipso Cp), 91.1 (β-η^5-Cp), 85.8 (α-η^5-Cp), 85.3 (H9-η^1:η^5-Cp), 83.9 (β-η^5-Cp), 83.9 (α-η^5-Cp), 82.2 (C8 or C10-η^1:η^5-Cp), 81.9 (C8 or C10-η^1:η^5-Cp), 26.2 (CH$_2$). MS: (EI) 491 (M$^+$), 456 (M$^+$–Cl), 435 (M$^+$–2CO). Anal. Found: C, 36.81; H. 1.81. C$_{15}$H$_9$ClO$_4$Ru$_2$. Theory: C, 36.66; H, 1.83%.

Microscale photolysis of III in CCl$_4$ for 4 h using an Ace Hanovia lamp, resulted in the precipitation of an orange solid from the reaction mixture. IR and ^{1}H NMR showed this solid to be identical to [Ru(CO)$_2$Cl]$_2$(η^5, η^5-C$_5$H$_4$CH$_2$C$_5$H$_4$). Removal of solvent from the reaction mixture and chromatography as described above gave VIII as the sole additional reaction product.

When solutions of the hydride, VII, were exposed to air, a red precipitate formed quickly. This red solid does not melt up to 300 °C. The compound is poorly soluble in all common solvents. IR: (CH$_2$Cl$_2$) 1945, 1766 cm^{-1}. ^{1}H NMR: (CDCl$_3$) 6.44 (q, 1H, Cp), 5.97 (q, 1H, Cp), 5.42 (q, 1H, Cp), 5.43 (q, 1H, Cp), 4.98 (t, 1H, Cp), 4.76 (m, 1H, Cp), 3.29 and 2.34 (AB quarter, J_{A-B} = 16.2 Hz, 2H, CH$_2$), 2.33 (dd, 1H, Cp?). ^{13}C NMR: (CDCl$_3$) 200.1 (Ru–CO), 198.3 (Ru–CO), 128.9 (ipso Cp), 113.7 (ipso Cp), 101.6 (Cp), 98.5 (Cp), 95.7 (Cp), 94.2 (Cp), 91.7 (Cp), 85.8 (Cp), 84.0 (Cp), 70.8 (Cp), 25.6 (CH$_2$). Note: the ^{13}C NMR spectrum was of poor quality with low signal to noise. Only high confidence resonances are reported.

5.3. Photolysis of Ru$_2$(CO)$_4$(η^5,η^5-C$_5$H$_4$(CH$_3$)$_2$CC$_5$-H$_4$), IV

An NMR sample of IV was prepared by dissolving the compound in C$_6$D$_6$ then degassing the solution with three freeze–pump–thaw cycles. The sample was placed in a Pyrex water jacket and photolyzed using a 350 W

high pressure UV lamp for 24 min. ^{1}H NMR: (C$_6$D$_6$) 4.94 (1H, Cp), 4.76 (1H, Cp), 4.73 (1H, Cp), 4.68 (1H, Cp), 4.67 (1H, Cp), 4.50 (1H, Cp), 4.33 (1H, Cp), 1.25 (3H, CH$_3$), 0.95 (3H, CH$_3$), −10.23 (s, 1H, Ru–H). ^{13}C NMR: (C$_6$D$_6$) 203.3 (Ru–CO), 200.1 (Ru–CO), 199.5 (2 C, Ru(CO)$_2$H), 143.8 (ipso Cp), 137.9 (ipso Cp), 100.0 (ipso Cp), 91.8 (Cp), 88.8 (Cp), 84.4 (Cp), 84.0 (Cp), 82.9 (Cp), 82.0 (Cp), 81.2 (Cp), 35.6 (C(CH$_3$)$_2$), 34.5 (CH$_3$), 29.7 (CH$_3$).

Photolysis of a 100 mg sample of IV in 3:1 C$_6$H$_6$:CHCl$_3$ in a Pyrex vessel for 30 min using a 350 W high pressure Hg lamp gave a red-orange solution. After removal of solvent, the solid was chromatographed on alumina using 1:1 petroleum ether:dichloromethane as an eluant. An intense yellow band was eluted from the column which gave IX in quantitative yield. Physical and spectral properties of IX prepared in this manner were identical to a sample recovered as a by-product of the reaction of (CH$_3$)$_2$C(C$_5$H$_4$Tl)$_2$ with [Cl$_2$Ru(CO)$_3$]$_2$ and reported previously [7b].

5.4. Photochemical studies of Ru$_2$(CO)$_4$(η^5,η^5-C$_5$H$_4$-C$_2$H$_4$C$_5$H$_4$), V

Photolysis of an NMR sample of V in C$_6$D$_6$ for 50 min at room temperature resulted in the appearance of Ru–H resonances at −10.38 and −17.34 ppm and a complex set of resonances in the ring and ethylene bridge regions. IR of the solution showed product bands at 2032, 2028, and 1976 cm^{-1}. Upon addition of dichloromethane to the photolysis solution, new IR bands were found at 2045, 2033, and 1988 cm^{-1}. HPLC of the products of this reaction contained one major product band (which was subsequently shown to be X by comparison with an authentic sample) and a second, lesser band whose identity has not yet been established.

A 10 mg sample of V in neat CHCl$_3$ in a microphotolysis cell was photolyzed for 30 min using a 350 W high pressure Hg lamp. After removal of solvent, the resulting red solid was separated by chromatography on alumina using 1:1 petroleum ether:dichloromethane as an eluant. The first yellow band was collected and stripped of solvent to give X as an orange crystalline solid. IR: (CDCl$_3$) 2042, 2032, 1978 cm^{-1}. ^{1}H NMR: (CDCl$_3$) 5.42 (m, 2H, Cp), 5.37 (q, 1H, Cp), 5.33 (t, 1H, Cp), 5.20 (q, 1H, Cp), 5.15 (q, 1H, Cp), 4.68 (t, 1H, Cp), 2.76 (ddd, J_{1-2} = 4.0 Hz, J_{1-3} = 3.3 Hz, J_{1-4} = 14.6 Hz, 1H, H-1), 2.62 (ddd, J_{2-3} = 15.3 Hz, J_{2-4} = 3.1 Hz, 1H, H-2), 2.33 (ddd, J_{3-4} = 12.2 Hz, 1H, H-3), 2.17 (ddd, 1H, H-4). ^{13}C NMR: (CDCl$_3$) 199.2 (Ru–CO), 198.1 (Ru–CO), 198.1 (2C, Ru–CO), 117.4 (ipso Cp), 116.7 (ipso Cp), 109.3 (ipso Cp), 89.5 (Cp), 88.8 (Cp), 87.9 (Cp), 87.1 (Cp), 85.6 (Cp), 85.4

(Cp), 76.1 (Cp), 29.2 (C–H-2, H-3), 24.7 (C–H-1, H-4).

The second yellow band from the column was isolated and stripped of solvent to gave a trace of [$Ru(CO)_2Cl]_2(\eta^5,\eta^5$-$C_5H_4CH_2C_5H_4$) as a yellow solid. IR: (CH_2Cl_2) 2052, 2002 cm^{-1}. ^{1}H NMR: ($CDCl_3$) 5.29 and 5.11 (A_2B_2 triplets, 8H, Cp), 2.55 (s, 4H, C_2H_4). ^{13}C NMR: ($CDCl_3$) 195.8 (Ru–CO), 83.7 (Cp), 83.7 (*ipso* Cp), 81.9 (Cp), 26.0 (C_2H_4).

5.5. Photolysis of $Ru_2(CO)_4[\eta^5,\eta^5$-$C_5H_4(CH_3)_2SiC_5H_4]$, VI

NMR samples of **VI** were photolyzed in both C_6D_6 and $C_6D_5CD_3$ as solvents using the Ace Hanovia apparatus. Spectra recorded in the first 5–10 min of photolysis contained complex ring regions, new Me_2Si resonances at 0.59 and 0.33 ppm, and a Ru–H resonance at −10.41 ppm. Upon continued photolysis, ring resonances at 5.10, 4.88, 4.61 and 4.45 and a Me_2Si resonance at 0.60 ppm increased while resonances associated with the hydride species decreased. After 2 h of photolysis only traces of the Ru–H species could be observed. Removal of solvent followed by chromatography on a 10 cm × 3 mm alumina column with 1:1 petroleum ether:dichloromethane as an eluant recovered **XII** as a pale yellow oil. IR: (CH_2Cl_2) 2032, 1999, 1973, 1937 cm^{-1}. ^{1}H NMR: (C_6D_6) 5.10 (t, 2H, Cp), 4.88 (t, 2H, Cp), 4.61 (t, 2H, Cp), 4.45 (t, 2H, Cp), 0.60 (s, 6H, Me_2Si). MS: (EI) 500 (M$^+$), 472 (M$^+$–CO), 444 (M$^+$–2CO), 416 (M$^+$–3CO), 388 (M$^+$–4CO).

Similar NMR-scale photolyses were carried out using optical filters ($\lambda < 450$ nm) and $400 < \lambda < 500$ nm) without affecting the observed results. A sample of **VI** in $C_6D_5CD_3$ was photolyzed for 5 min and shown by NMR to contain both hydride and **XII**. After storage overnight in the dark, the sample showed complete decomposition of hydride, but no change in the relative amounts of **VI** and **XII**. In a similarly prepared sample, the hydride was decomposed after 5 min in a 65 °C bath with no change in the relative amounts of **VI** and **XII**.

Photolysis of **VI** in neat CCl_4 resulted in the precipitation of [$Ru(CO)_2Cl]_2[\eta^5,\eta^5$-$C_5H_4(CH_3)_2SiC_5H_4]$ as a tan solid. IR: (CH_2Cl_2) 2055, 2005 cm^{-1}. ^{1}H NMR: ($CDCl_3$) 5.60 and 5.44 (A_2B_2 triplets, 8H, Cp), 0.63 (s, 6H, Me_2Si, $J_{Si-H} = 6.8$ Hz). ^{13}C NMR: ($CDCl_3$) 195.6 (Ru–CO), 99.4 (Cp), 88.4 (*ipso* Cp), 85.3 (Cp), 0.16 (Me_2Si).

Removal of solvent from the photolysis mixture yielded a yellow oil which was chromatographed on alumina to give **XI** as a yellow oil which formed a waxy, yellow solid after being placed under vacuum overnight, m.p. 156–157 °C. IR: (CH_2Cl_2) 2046, 2035, 1984 cm^{-1}. ^{1}H NMR: ($CDCl_3$) 5.80 (m, 2H, α-η^5-Cp), 5.55 (m, 1H, β-η^5-Cp), 5.42 (m, 1H, β-η^5-Cp), 5.15 (m, 1H, H-8 or H-10, η^5:η^1-Cp), 5.12 (m, 1H, H-9,

η^5:η^1-Cp), 5.09 (m, 1H, H-8 or H-10, η^5:η^1-Cp), 0.63 (s, 3H, Me–Si, $J_{Si-H} = 7.1$ Hz), 0.47 (s, 3H, Me–Si, $J_{Si-H} = 6.9$ Hz). ^{13}C NMR: ($CDCl_3$) 198.6 (Ru–CO), 197.7 (Ru–CO), 197.5 (2C, Ru–CO), 137.9 (*ipso* Cp), 113.3 (*ipso* Cp), 108.6 (*ipso* Cp), 94.8 (α-η^5-Cp), 92.6 (C-8 or C-10, η^5:η^1-Cp), 91.9 (C-8 or C-10, η^5:η^1-Cp), 90.9 (α-η^5-Cp), 88.7 (β-η^5-Cp), 88.6 (β-η^5-Cp), 82.3 (C-9, η^5:η^1-Cp), 0.13 (Me–Si), −2.13 (Me–Si).

XI could be prepared in quantitative yield by photolysis of **VI** in 4:1 benzene:chloroform followed by workup as described above.

5.6. Crystal structure determination

A summary of crystallographic data is given in Table 1. A crystal of **VIII** was mounted with epoxy cement on glass fibers. Unit-cell parameters were obtained by the least squares refinement of the angular settings of 24 reflections ($20° \leq 2\Theta \leq 25°$). Photographic evidence determined that the crystal belonged to a monoclinic system. Systematic absences in the diffraction data indicated either of the C-centered space groups $C2/c$ or Cc. The noncentrosymmetric alternative, Cc, was first suggested by the E-statistics (e.g. $|E^2 - 1| = 0.74$) and confirmed by the results of refinement. The resulting two independent molecules of **VIII** are nearly identical.

The structure was solved by direct methods and completed by subsequent difference Fourier synthesis. All non-hydrogen atoms were anisotropically refined, and all hydrogen atoms were treated as idealized, updated isotropic contributions (dCH = 0.96 Å), SHELXTL (5.1) software was used on all calculations [13].

Acknowledgements

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