$C_5Me_5)Ru(NO)]$, 108419-26-7; 1,2-dichloroethane, 107-06-2.

Supplementary Material Available: Tables giving complete details of the structure determination of complex **4** including crystal, data collection, and refinement parameters, fractional atomic coordinates, equivalent isotropic thermal parameters, bond lengths, bond angles, planes, anisotropic displacement parameters, and H-atom coordinates (4 pages); listing of structure factors (10 pages). Ordering information is given on any current masthead page.

Carbon–Carbon Double Bond Formation from a *cis*-Bis(chloromethyl) Complex

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Abstract: The complexes $Cp^*Ru(NO)(CH_2Cl)Cl$ and $Cp^*Ru(NO)(CH_2Cl)_2$ are formed in a stepwise fashion by treating $Cp^*Ru(NO)Cl_2$ with ethereal diazomethane in the presence of Cu powder ($Cp^* = \eta^5\text{-}C_5Me_5$). Photolysis or thermolysis of $Cp^*Ru(NO)(CH_2Cl)_2$ leads to the formation of ethylene and the reformation of $Cp^*Ru(NO)Cl_2$. Deuterium labeling studies show the ethylene to originate by an *intramolecular* coupling of CH_2 groups. An X-ray analysis of $Cp^*Ru(NO)(CH_2Cl)_2$ reveals a nearly symmetric C_s molecular geometry, with a "vertical" face-to-face orientation of the *cis*-bis(chloromethyl) ligands. The (C–Ru–C) angle of 79.4 (5)° between the chloromethyl ligands is somewhat acute, placing the nonbonded methylene carbon atoms at a separation of 2.68 Å: monoclinic space group $P2_1/n$, $a = 7.083$ (4) Å, $b = 17.723$ (4) Å, $c = 12.055$ (5) Å; $\beta = 94.27$ (4)°; $R/R_w = 5.50\%/5.50\%$. ^1H NOE NMR experiments on the bis(chloromethyl) complex indicate that the "vertical" chloromethyl methylene orientation seen in the solid state is also preferred in solution. The mechanistic aspects of ethylene extrusion are discussed in terms of a transition state, where one CH_2Cl ligand undergoes migratory insertion to an "ionized" chloromethyl ligand, represented as $Ru = CH_2^{\delta+}Cl^{\delta-}$. The β-chloroethyl complex $Cp^*Ru(NO)Cl(CH_2CH_2Cl)$ expected from this process is apparently unstable to β-Cl elimination, leading to ethylene extrusion and the reformation of $Cp^*Ru(NO)Cl_2$. Frontier orbital analysis based on the established theory of the $CpRu(NO)R_2$ system suggests that the observed face-to-face orientation of the chloromethyl ligands is conducive to the migratory insertion. A filled metal $d\pi$ orbital is correctly oriented for stabilizing the metal–methylidene-like $Ru = CH_2^{\delta+}Cl^{\delta-}$ interaction in the transition state.

Introduction

Transition-metal three-legged piano-stool complexes containing *cis*-dialkyl or diaryl ligands have been the subject of fundamental research on metal-mediated carbon–carbon bond formation. In dialkyl complexes where the third cis ligand is CO or NO, alkyl migratory insertion to CO or NO can be a significant form of reactivity in addition to direct reductive elimination of a C–C bond. Such is the case for the reactive complex $CpCo(CO)(CH_3)_2$, where acetone is formed ($Cp = \eta^5\text{-}C_5H_5$).[2] For the isoelectronic Fe and Ru nitrosyl complexes $CpM(NO)(CH_3)_2$ and $Cp^*M(NO)(CH_3)_2$, carbon–nitrogen bond formation occurs, leading to oximato, carboxamido, and cyano complexes ($Cp^* = \eta^5\text{-}C_5Me_5$).[3]

While there are a number of known piano-stool complexes containing halomethyl ligands,[4] up until now related *cis*-bis(halomethyl) complexes have not been reported. Recently, a number of square-planar *cis*-(alkyl)(halomethyl) and *cis*-bis(halomethyl) complexes of Pd(II) and Pt(II) have been reported.[5] Interestingly, the reactivity for some of these complexes has been proposed as a model for the polymerization of diazomethane by transition metals.[5d] Specifically, it was proposed that migratory insertion of a halomethyl ligand into an "ionized" $M{=}CH_2^+X^-$ ligand leads to carbon–carbon bond formation. However, no further reports elaborating this proposed mechanism have yet appeared.

Our present report deals with a comprehensive discussion of the structure, bonding, and reactivity of $Cp^*Ru(NO)(CH_2Cl)_2$, a new *cis*-bis(chloromethyl) complex which reacts smoothly to extrude ethylene and regenerate the parent $Cp^*Ru(NO)Cl_2$ complex. Drawing from the results of earlier reactivity studies of complexes containing the $Cp^*Ru(NO)$ core[3b,6,7] and the results of published theoretical discussions of the $CpM(NO)R_2$ framework,[8] we are able to present a consistent mechanism for the

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observed C–C double bond formation from this *cis*-bis(chloromethyl) complex.

Results and Discussion

Halomethyl Complex Formation. Under conditions similar to those we reported for the synthesis of $CpCr(NO)_2CH_2Cl$,[4e,f] CH_2Cl_2 solutions of $Cp^*Ru(NO)Cl_2$ are converted in a stepwise fashion to $Cp^*Ru(NO)(CH_2Cl)Cl$ and $Cp^*Ru(NO)(CH_2Cl)_2$ by the dropwise addition of ethereal CH_2N_2 in the presence of Cu powder (eq 1). The reaction can also be carried out in THF or Et₂O with equal success. By virtue of the fact that no methylene insertion occurs in the absence of Cu powder, we postulate that the generation of a reactive Cu–methylene species is critical to the formation of chloromethyl products. Rapid addition of CH_2N_2 results in the inhibition of the reaction, presumably caused by extensive polymethylene buildup on the Cu surface. Recent matrix isolation work, showing the formation of $Cu{=}CH_2$ groups upon the addition of CH_2N_2 to elemental Cu,[9] suggests that methylene insertion into the metal–chloride bond may be possible when the Ru–chloride complex comes into contact with the Cu surface.

$$Cp^*Ru(NO)Cl_2 \xrightarrow[CH_2Cl_2]{CH_2N_2/Cu} Cp^*Ru(NO)(CH_2Cl)Cl \xrightarrow[CH_2Cl_2]{CH_2N_2/Cu} Cp^*Ru(NO)(CH_2Cl)_2 \quad (1)$$

Isolation and Properties of $Cp^*Ru(NO)(CH_2Cl)Cl$. The fact that both $Cp^*Ru(NO)(CH_2Cl)Cl$ and $Cp^*Ru(NO)(CH_2Cl)_2$ are produced in the CH_2N_2/Cu reaction presents a minor separation problem in the isolation of pure $Cp^*Ru(NO)(CH_2Cl)Cl$. Since attempts to chromatograph either chloromethyl complex on normally available alumina or silica gel supports result in significant decomposition, our best method of isolating pure $Cp^*Ru(NO)(CH_2Cl)Cl$ from the CH_2N_2/Cu route involves a very brief addition of CH_2N_2 to the starting dichloride complex. The resulting product is mostly $Cp^*Ru(NO)(CH_2Cl)Cl$, which is easily separated from the insoluble dichloride by extraction into warm hexane. Traces of $Cp^*Ru(NO)(CH_2Cl)_2$ present are removed by a single recrystallization from hexane, leaving air-stable, orange-brown crystals of $Cp^*Ru(NO)(CH_2Cl)Cl$ in 69% yield (based on recovered starting material).

The $Cp^*Ru(NO)(CH_2Cl)Cl$ complex has been previously identified as a product from the thermolysis of $Cp^*Ru(NO)Ph_2$ in CH_2Cl_2.[6] Indeed, the spectral characterization of $Cp^*Ru(NO)(CH_2Cl)Cl$ produced from our diazomethane/Cu reaction closely resembles the partially characterized product reported by Bergman and Chang. The complex displays an intense IR absorption at 1775 cm^{-1} in CH_2Cl_2 indicative of a terminal nitrosyl ligand. The 15-cm^{-1} reduction in ν_{NO} from the starting dichloride complex suggests the chloromethyl ligand to be a slightly stronger σ-donating ligand than a chloro ligand. The ^1H NMR spectrum shows a single resonance for the η^5-C_5Me_5 ligand and the diastereotopic methylene protons appear as an AX pattern ($\Delta\delta_{AX}$ = 2.1 ppm; $^2J_{AX}$ = 7.1 Hz). In the ^{13}C NMR spectrum, the expected resonances for the skeletal and methyl carbons of the η^5-C_5Me_5 ligand are present as well as a resonance at δ 42.9 ($^1J_{CH}$ = 159 Hz) characteristic of the chloromethyl ligand.

Isolation and Properties of $Cp^*Ru(NO)(CH_2Cl)_2$. Preparation of $Cp^*Ru(NO)(CH_2Cl)_2$ from the CH_2N_2/Cu reaction is quite facile. In order to assure complete conversion to the bis(chloromethyl) complex, two additions of CH_2N_2 are carried out, each time utilizing fresh Cu powder. Extraction and recrystallization of the crude product in hexane gives $Cp^*Ru(NO)(CH_2Cl)_2$ as orange, air stable crystals in 95% yield. Solutions of the complex in nitromethane show no significant conductivity.

The bis(chloromethyl) complex displays an intense IR absorption at 1760 cm^{-1}, a value 15 cm^{-1} lower than that seen for $Cp^*Ru(NO)(CH_2Cl)Cl$. The additive effect of the second chloromethyl ligand increases the back-donation to the nitrosyl ligand, shifting ν_{NO} to lower energy. A comparable trend in ν_{NO} is observed from $Cp^*Ru(NO)Cl_2$ to $Cp^*Ru(NO)(CH_3)Cl$ to $Cp^*Ru(NO)(CH_3)_2$,[10] noting that two methyl ligands are significantly more donating than two chloromethyl ligands.

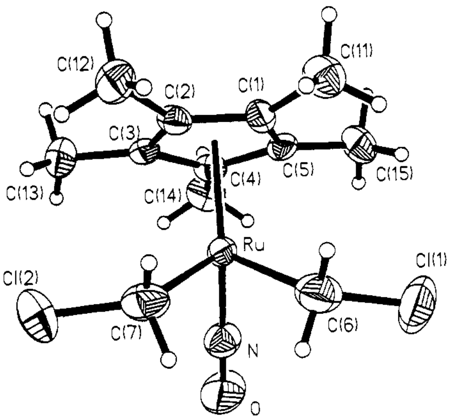

Figure 1. Molecular structure of $Cp^*Ru(NO)(CH_2Cl)_2$.

Table I. Selected Geometric Data for $Cp^*Ru(NO)(CH_2Cl)_2$

Bond Lengths, (Å)			
Ru–N	1.74 (1)	Ru–C(4)	2.25 (1)
N–O	1.17 (2)	Ru–C(5)	2.29 (1)
$Ru{-}Cp_{(cent)}$	1.93	Cl(1)–C(6)	1.80 (2)
C(6)--C(7)	2.68	Cl(2)–C(7)	1.74 (1)
Bond Angles, (deg)			
Ru–N–O	174.9 (9)	N–Ru–C(7)	95.4 (5)
Ru–C(7)–Cl(2)	116.5 (7)	N–Ru–C(6)	93.4 (5)
Ru–C(6)–Cl(1)	114.7 (7)	C(7)–Ru–C(6)	79.4 (5)
$Cp_{(cent)}{-}Ru{-}N$	132.9	N–Ru–C(1)	152.2 (4)
$Cp_{(cent)}{-}Ru{-}C(6)$	120.9	C(1)–C(2)–C(3)	108.5 (9)
$Cp_{(cent)}{-}Ru{-}C(7)$	121.0	C(2)–C(3)–C(4)	107.5 (9)
C(3)–C(4)–C(5)	108.5 (9)	C(1)–C(5)–C(4)	105.6 (9)
C(2)–C(1)–C(5)	109.8 (9)		
Torsion Angles, (deg)			
$Cp_{(cent)}{-}Ru{-}C(6){-}Cl(1)$	73.3	$Cp_{(cent)}{-}Ru{-}N{-}O$	2.6
$Cp_{(cent)}{-}Ru{-}C(7){-}Cl(2)$	−78.3	N–Ru–C(6)–Cl(1)	−74.3
N–Ru–C(7)–Cl(2)	66.8		
Least-Squares Planes			
plane 1:	C(1)–C(2)–C(3)–C(4)–C(5)	(0.007 Å mean dev)	
plane 2:	$Cp_{(cent)}{-}Ru{-}N{-}O$	(0.003 Å mean dev)	
plane 3:	Cl(1)–C(6)–Ru–C(7)–Cl(2)	(0.2 Å mean dev)	
Angles between Least-Squares Planes, (deg)			
plane 1 and plane 2:	90.2	plane 1 and plane 3:	46.5
plane 2 and plane 3:	93.1		

The ^1H NMR spectrum of $Cp^*Ru(NO)(CH_2Cl)_2$ shows a single resonance for the η^5-C_5Me_5 ligand with the diastereotopic methylene protons appearing as an AX pattern ($\Delta\delta_{AX}$ = 0.79 ppm; $^2J_{AX}$ = 7.5 Hz). The ^{13}C NMR spectrum shows signals characteristic for the skeletal and methyl group carbons of the Cp* ring as well as a resonance at δ 43.5 for the chloromethyl carbons ($^1J_{CH}$ = 145 Hz).

Structure of $Cp^*Ru(NO)(CH_2Cl)_2$. The molecular structure of $Cp^*Ru(NO)(CH_2Cl)_2$ is shown in Figure 1. Table I lists selected geometric data for the complex. With no crystallographically imposed symmetry, the molecule adopts a piano-stool geometry with nearly C_s molecular symmetry. The plane of the skeletal Cp* carbon atoms is almost exactly perpendicular to the plane defined by the $Cp^*_{centroid}{-}Ru{-}N{-}O$. The nitrosyl ligand is bound in an essentially linear fashion, with ∠Ru–N–O = 175°. The atoms Cl(1)–C(6)–Ru–C(7)–Cl(2) deviate from planarity by only 0.2 Å, with their plane lying nearly perpendicular to the plane defined by $Cp^*_{(centroid)}{-}Ru{-}N{-}O$. The C(6)–Ru–C(7) angle of 79.4 (5)° is considerably compressed from the C(6)–Ru–N and

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[9] Chang, S. C.; Kafafi, Z. H.; Hauge, R. H.; Billups, W. E.; Margrave, J. L. *J. Am. Chem. Soc.* **1987**, *109*, 4508.

[10] $Cp^*Ru(NO)Cl_2$: $\nu_{NO}(CH_2Cl_2)$ = 1792 cm^{-1}. $Cp^*Ru(NO)(CH_3)Cl$: $\nu_{NO}(CH_2Cl_2)$ = 1762 cm^{-1}. $Cp^*Ru(NO)(CH_3)_2$: $\nu_{NO}(CH_2Cl_2)$ = 1722 cm^{-1}.

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C(7)–Ru–N angles, resulting in a nonbonded separation between the methylene carbons of 2.68 Å. The average Ru–methylene carbon distance in the complex is 2.10 Å, falling in the short end of the range typical for Ru^{II}–C single-bond distances.[13] The average ∠Ru–C–Cl of 115.6° is in the range found for other halomethyl complexes,[4f,g] and the C–Cl distances are quite normal.

The most notable structural feature of $Cp^*Ru(NO)(CH_2Cl)_2$ is the close fac-to-face orientation of the chloromethyl ligands. Similar face-to-face orientations are observed in *cis*-(dibenzyl) or *cis*-bis(CH_2SiMe_3) three-legged-stool complexes and are consistent with the steric demands of the α-substituents.[8,11,12] However, the nonbonded C(6)-C(7) separation in the bis(chloromethyl) complex is 0.12 Å closer than that found in $Cp^*Re(O)(CH_2Ph)_2$ and 0.76 Å closer than that in $CpW(NO)(CH_2SiMe_3)_2$, indicating that the C–M–C angle is not just a function of steric effects. The X-ray structure of $Cp^*Ru(NO)Et_2$ shows a (Et–Ru–Et) angle of 81.6 (6)° and a nonbonded C- -C methylene separation of 2.78 Å, indicating that the chloromethyl ligands alone are not uniquely influencing the geometry.[14]

The application of difference NOE ^1H NMR techniques to the bis(chloromethyl) complex is valuable for assessing the orientation of the chloromethyl ligands in solution. A 10-fold enhancement of the upfield methylene signal (H_a) relative to the downfield methylene signal (H_b) is found when the sample is irradiated at the resonant frequency for the Cp* methyl groups. This evidence strongly supports a "vertical" methylene orientation, where the H_a protons are in closer proximity to the ring than the H_b protons, similar to the conformation seen in the solid state. Using the X-ray structure as a basis for approximation, we estimate that the closest approach of the H_a protons to the Cp*-methyl protons to be roughly 2.5 Å compared to a distance of around 4 Å for the H_b protons. It is likely that the close proximity of the two chloromethyl ligands together with their large cone angle prevents complete rotational freedom about the Ru–C bonds, thus limiting the chloromethyl ligand rotation to a rocking pattern where the H_b protons never get very close to the Cp*-methyl protons.

Thermal and Photochemical Reactivity of $Cp^*Ru(NO)(CH_2Cl)Cl$. In a manner similar to that of several reported halomethyl complexes,[4] the thermal and photochemical reactivity of $Cp^*Ru(NO)(CH_2Cl)Cl$ is dominated by the formation of polymethylene and the reformation of the starting dichloride complex (eq 2). In the solid state, $Cp^*Ru(NO)(CH_2Cl)Cl$ undergoes decomposition without melting over the range 148–155 °C. Analysis of the solid residue by IR and ^1H NMR spectroscopy shows the presence of $Cp^*Ru(NO)Cl_2$ as the only identifiable organometallic product with the presence of oligomeric polymethylene being indicated by its characteristic ^1H NMR resonances at δ 0.88 and 1.25. IR analysis of the head-space gases released upon thermolysis shows no evidence of ethylene or other small molecule products. Heating C_6D_6 solutions of $Cp^*Ru(NO)(CH_2Cl)Cl$ at 70 °C for 12 h results in the darkening of the solution and the appearance of a flocculent, milky-white precipitate. Analysis of the solution by ^1H NMR spectroscopy indicates an approximately 1:1 mixture of the starting chloromethyl complex and $Cp^*Ru(NO)Cl_2$, together with signals that are attributable to soluble polymethylene oligomers. Mercury lamp photolysis of $Cp^*Ru(NO)(CH_2Cl)Cl$ in C_6D_6 for 10 min at 20 °C gives results almost identical to those of the thermolysis experiments.

$$Cp^*Ru(NO)(CH_2Cl)Cl \xrightarrow{\Delta \text{ or } h\nu} Cp^*Ru(NO)Cl_2 + \text{-}(CH_2)_x\text{-} \quad (2)$$

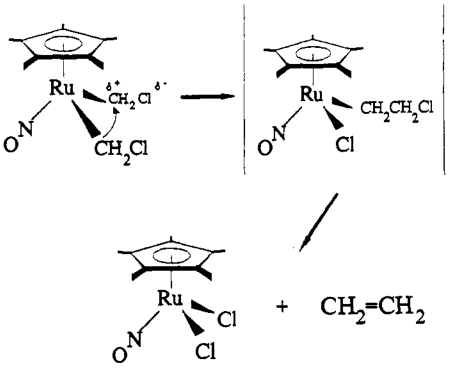
Thermolysis and Photolysis of $Cp^*Ru(NO)(CH_2Cl)_2$. The $Cp^*Ru(NO)(CH_2Cl)_2$ complex melts sharply in the air at 70–72 °C with no detectable decomposition until the temperature reaches 100 °C. Above 100 °C the orange melt begins to evolve gas bubbles, and by 130 °C the material turns dark green and solidifies. Examination of the solid green residue by IR and ^1H NMR spectroscopy shows the presence of the starting dichloride complex and only small signals attributed to polymethylene oligomers. No traces of the $Cp^*Ru(NO)(CH_2Cl)Cl$ complex are detectable. Gas-phase IR analysis of the gaseous byproducts reveals only the presence of ethylene (eq 3). As monitored by ^1H NMR spectroscopy, photolysis of a C_6D_6 solution of $Cp^*Ru(NO)(CH_2Cl)_2$ at 20 °C in an NMR tube results in the formation of a clear green solution containing $Cp^*Ru(NO)Cl_2$ and ethylene. Photolysis of $Cp^*Ru(NO)(CH_2Cl)_2$ in $CDCl_3$ or hexane also produces ethylene and $Cp^*Ru(NO)Cl_2$ with similar ease. Addition of 2 equiv of [PPN]Cl to $CDCl_3$ solutions of $Cp^*Ru(NO)(CH_2Cl)_2$ has no measurable effect on the ease of ethylene formation.

$$Cp^*Ru(NO)(CH_2Cl)_2 \xrightarrow{\Delta \text{ or } h\nu} Cp^*Ru(NO)Cl_2 + CH_2{=}CH_2 \quad (3)$$

The results of deuterium crossover experiments shown in eq 4 address the origin of the ethylene produced in eq 3. As determined by gas-phase IR analysis, the thermolysis of equimolar amounts of $Cp^*Ru(NO)(CH_2Cl)_2$ and $Cp^*Ru(NO)(CD_2Cl)_2$ leads to the formation of $CH_2{=}CH_2$ and $CD_2{=}CD_2$, with the only $CH_2{=}CD_2$ produced being that from the ca. 15% $Cp^*Ru(NO)(CH_2Cl)(CD_2Cl)$ impurity present in our deuterated complex.[15] These experiments lead us to conclude that ethylene formation arises by an *intramolecular* coupling of the chloromethyl ($-CH_2-$) fragments.

$$Cp^*Ru(NO)(CH_2Cl)_2 + Cp^*Ru(NO)(CD_2Cl)_2 \xrightarrow{\Delta} Cp^*Ru(NO)Cl_2 + CH_2{=}CH_2 + CD_2{=}CD_2 \text{ (no crossover)} \quad (4)$$

Possible Mechanism for Ethylene Extrusion. Our discussion of a coupling mechanism leading to the formation of ethylene begins with McCrindle's work on square-planar *cis*-alkyl(halomethyl) Pd(II) and Pt(II) complexes.[5] In keeping with the expected lability of the α-halo substituent,[4f] it can be argued that the transition state leading to the formation of a new carbon–carbon bond involves a polarized chloromethyl ligand, represented as $Ru{=}CH_2^{\delta+}Cl^{\delta-}$. Chloromethyl migration to the metal–methylidene-like $Ru{=}CH_2^{\delta+}$ moiety would be expected to produce a β-chloroethyl ligand, and β-chloride elimination would be expected to lead to ethylene and the reformation of the cis metal–dihalide complex (eq 5). The fact that the ease of ethylene formation is not solvent dependent together with the fact that added [PPN]Cl to $CDCl_3$ solutions of $Cp^*Ru(NO)(CH_2Cl)_2$ does not measureably suppress ethylene formation indicates that formal



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(13) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1-S83.

(14) X-ray data for $Cp^*Ru(NO)(CH_2CH_3)_2$: triclinic space group $P\bar{1}$, a = 7.475 (4) Å, b = 8.605 (4) Å, c = 12.066 (4) Å, α = 82.28 (3)°, β = 78.97 (3) °, γ = 81.45 (4)°, V = 748.9 (6) $Å^3$, Z = 2, d_{calc} = 1.439 g cm^{-3}, T = 193 K, Mo Kα radiation, μ = 1.013 mm^{-1}, $F(000)$ = 336 e^-, R/R_w = 4.16%/4.87% for 1632 data ($F > 3\sigma(F)$). 154 parameters refined, goodness-of-fit = 1.35; average ($Ru-CH_2CH_3$) bond length = 2.13 Å, Ru–N = 1.722 (6) Å, N–O = 1.183 Å, ∠Ru–N–O = 175.8 (6)°.

(15) The examination the IR region between 1050 and 650 cm^{-1} is particularly diagnostic for the detection of the isotopomers of ethylene: (a) Crawford, B. L., Jr.; Lancaster, J. E.; Inskeep, R. G. *J. Chem. Phys.* **1953**, *21*, 678. (b) Tables of *Molecular Vibrational Frequencies Consolidated*; Shimanouchi, T., Ed.; National Bureau of Standards, U.S. Government Printing Office: Washington, DC, 1972; Vol. 1.

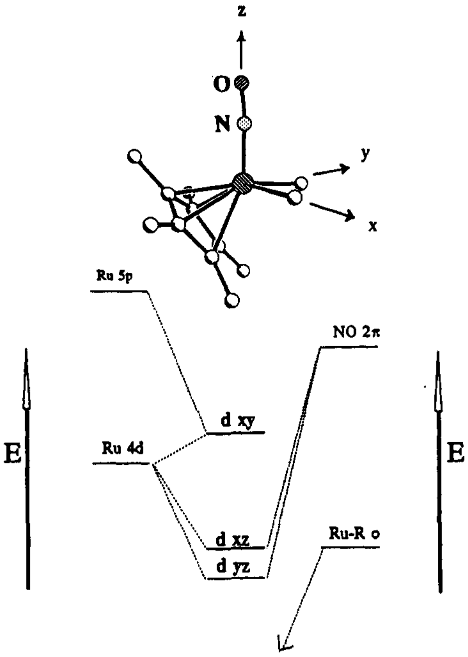


Figure 2. Molecular orbital diagram for $Cp^*Ru(NO)R_2$ (based on ref 8).

chloromethyl ionization in the ground state is not implicated. This is consistent with the hexane solubility (i.e., nonpolar nature) of the $Cp^*Ru(NO)(CH_2Cl)_2$ complex and its nonelectrolytic behavior in CH_3NO_2.

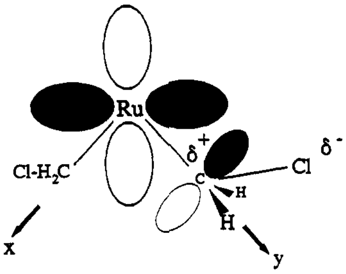
Independent experiments stemming from chlorocarbon trapping of the 16-electron $[Cp^*Ru(NO)]$ transient reveal important information regarding possible intermediates along the path of ethylene extrusion from $Cp^*Ru(NO)(CH_2Cl)_2$.[7] Attempts to generate $Cp^*Ru(NO)(CH_2CH_2Cl)Cl$ by oxidative addition of a C–Cl bond of 1,2-dichloroethane to the $[Cp^*Ru(NO)]$ transient have failed, leading instead to the formation of ethylene and a dinuclear complex arising from the oxidative addition of $Cp^*Ru(NO)Cl_2$ to a $[Cp^*Ru(NO)]$ transient (eq 6). Thus, a

$$Cp^*Ru(NO)Ph_2 + Cl{-}CH_2CH_2{-}Cl \rightarrow [Cp^*Ru(\mu\text{-}NO)Cl]_2 + CH_2{=}CH_2 + Ph{-}Ph \quad (6)$$

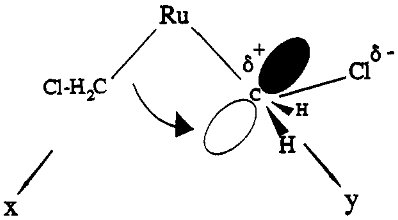
β-chloroethyl complex $[Cp^*Ru(NO)(CH_2CH_2Cl)Cl]$ produced by chloromethyl migration to a $Ru{=}CH_2^{\delta+}Cl^{\delta-}$ ligand can be expected to undergo β-chloride elimination to liberate ethylene (eq 5).

Electronic Structure Requirements for C–C Bond Formation. Molecular orbital studies have contributed a great deal to our understanding of intramolecular bond formation in organometallic complexes.[16] A previously published valence orbital analysis of the $CpRu(NO)Me_2$ complex identifies the highest occupied orbitals to be the d^6 "metal" levels of "$(t_{2g})^6$" parentage.[8] Treating the $Cp^*Ru(NO)(CH_2Cl)_2$ complex as an analogue of the parent $CpRu(NO)Me_2$ complex, we use an orientation that places the Ru–NO vector along the positive z axis and the Ru–CH_2 bonds along the x and y axes. Thus, Figure 2 shows the HOMO of the $Cp^*Ru(NO)R_2$ system to be primarily the Ru d_{xy} orbital which is nonbonding with regard to the nitrosyl ligand. Importantly, the Ru d_{xz} and d_{yz} orbitals are expected to be stabilized well below the energy of the d_{xy} level due to strong nitrosyl π-acceptance along the z axis.

Starting from a face-to-face orientation, a transition state involving a partially ionized chloromethyl ligand $Ru{=}CH_2^{\delta+}$ would enjoy the stabilization from metal d_{xy} back-donation into the methylidene-like $p\pi$-acceptor level lying in the xy plane (A). Furthermore, because of its alignment in the xy plane, migration of the chloromethyl σ-bond into the $p\pi$ level of the $Ru{=}CH_2^{\delta+}$ moiety can be expected to be straightforward (B).[16] Chloromethyl ligand migration to NO is not expected to be favorable, since the methylidene-like $p\pi$ level on the $Ru{=}CH_2^{\delta+}$ moiety can be expected to be somewhat lower in energy than the nitrosyl π^*-acceptor levels.[16]

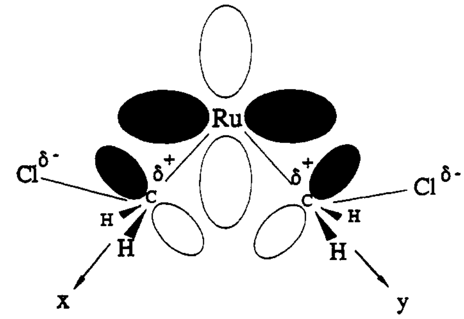


A



B

On the basis of the extra energy required to create a doubly "ionized" transition state, it is reasonable to rule out the likelihood of a cis-$Cp^*Ru(NO)({=}CH_2)_2^{+}2Cl^{-}$ species being involved in the formation of ethylene (C). Nevertheless, it is worth mentioning that the theory of Eisenstein and co-workers predicts the face-to-face methylene conformation to be the most favorable for direct carbon–carbon double bond elimination from cis-bis(carbene) complexes.[17] The strong competitive stabilization of the d_{xz} and d_{yz} orbitals by the nitrosyl ligand would be expected to discourage the reorientation of the methylidene-like $p\pi$-acceptor levels out of the xy plane.[18]



C

Concluding Remarks. The availability of the novel cis-bis(chloromethyl) complex $Cp^*Ru(NO)(CH_2Cl)_2$ provides a new experimental format for studying intramolecular carbon–carbon bond formation. In accord with previous studies of complexes containing only one halomethyl ligand, our present analysis of the reactivity of halomethyl complexes suggests the importance of considering transition states where significant interactions occur between strongly polarized halomethyl ligand ($-CH_2^{\delta+}Cl^{\delta-}$) and the filled $d\pi$ orbitals of the metal. We conclude that the face-to-face chloromethyl orientation is conducive for initial carbon–carbon bond formation, leading to a transition state which resembles alkyl migratory insertion to a methylidene ligand. We propose that initial carbon–carbon bond formation occurs when one chloromethyl ligand migrates to a methylidene-like $Ru{=}CH_2^{\delta+}Cl^{\delta-}$ group which is stabilized in the transition state by

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(17) Cauchy, D.; Jean, Y.; Eisenstein, O.; Volatron, F. *Organometallics* **1988**, *7*, 829.

(18) (a) Gladysz, J. A.; Tam, W.; Wong, W. K. *J. Am. Chem. Soc.* **1979**, *101*, 1589. (b) Herrmann, W. A.; Hubbard, J. L.; Bernal, I.; Korp, J. D.; Haymore, B. L.; Hillhouse, G. L. *Inorg. Chem.* **1984**, *23*, 2978.

back-donation from the filled Ru d_{xy} orbital. Subsequent ethylene formation is likely the result of spontaneous β-chloride elimination from the resulting β-(chloroethyl) complex. Investigations of the role of migratory insertion processes in related *cis*-(alkyl)(chloromethyl) and *cis*-(aryl)(chloromethyl) complexes are currently underway in our group.

Experimental Section

Standard Schlenk techniques employing an inert atmosphere (N_2 gas) were employed in all syntheses. Reagent grade solvents were purified by distillation from appropriate drying agents. The starting complex Cp*Ru(NO)Cl_2 was prepared as previously described.[7] Cu powder (electrolytic dust) was used as received from Fisher. Routine filtrations were performed through Analytical Filter Pulp (Schleicher and Schuell). [PPN]Cl was obtained from Aldrich. Infrared spectra were recorded on a Perkin-Elmer 1430 or Mattson Polaris FT spectrophotometer. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker WP-270 spectrometer at 270 and 67.9 MHz, respectively. Residual solvent peaks were used as internal standards (7.24 ppm [^{1}H] and 77.0 ppm [^{13}C] for $CDCl_3$; 7.15 ppm [^{1}H] and 128.0 [^{13}C] for C_6H_6). Mass spectra were obtained with a Finnigan 4610 mass spectrometer using chemical ionization (methane). Conductivity measurements were made on 1×10^{-3} M CH_3NO_2 solutions using a YSI Model 31A conductivity bridge. Melting points were measured with a mel-temp device (Laboratory Devices) in open capillaries and are uncorrected. Combustion analyses were performed by Robertson Laboratories, Inc. Madison, NJ.

Diazomethane (CH_2N_2) was generated using the "alcohol free" method from Diazald (Aldrich).[19] *Caution*: Diazomethane is exceedingly toxic and solutions have been known to explode unaccountably! All work must be carried out in a well-ventilated fume hood behind safety shields. The ethereal diazomethane was collected directly on to KOH pellets and was stored in a −60 °C dewar until use. Deuterated diazomethane was prepared in a two-phase reaction using ethereal MNNG (Aldrich) and 40% KOD in D_2O. After the generation of CD_2N_2 was finished (20 min), the ether layer was transferred by Teflon cannula to a clean flask and distilled into a fresh storage flask partially filled with dry Et_2O using minimum heat. Storage at −60 °C (*with no solid KOH*) resulted in the precipitation of residual water. The reservoir of CH_2N_2 (or CD_2N_2) was tapped with 0.5 mm i.d. Teflon cannula tubing (Rainin Corp.) and was pumped with a HAAKE BUCHLER peristaltic pump (Model No. 426-2000) equipped with a 20-cm section of 1.6 mm i.d. VITON tubing (Cole-Parmer). A second piece of Teflon tubing delivers the CH_2N_2 solution to the vented reaction vessel through a punctured rubber septum.

Synthesis of Cp*Ru(NO)(CH_2Cl)Cl. Cp*Ru(NO)Cl_2[7] (0.05 g, 0.15 mmol) was dissolved in 40 mL of CH_2Cl_2 together with 2 g of Cu powder and treated dropwise with ethereal diazomethane (ca. 1 mL/min) for 5–10 min with vigorous magnetic stirring, until the initial green color just changed to a brownish-orange color. Stirring was continued for another 5 min after diazomethane addition was ceased, and the mixture was filtered into a clean Schlenk tube. After removal of solvent in vacuo, the orange-brown residue was extracted with 20 mL of 50 °C hexane and refiltered into a small Schlenk tube. Concentration to 5 mL and crystallization at −40 °C gave 0.03 g (0.08 mmol) of analytically pure Cp*Ru(NO)(CH_2Cl)Cl. The yield of this reaction, based on the recovery of 0.01 g of Cp*Ru(NO)Cl_2 from the hexane insoluble residue, was 69%. ^{1}H NMR (C_6D_6): δ 5.99 (d, 1 H, CH_aH_bCl, $J_{ab} = 7.1$ Hz), δ 3.89 (d, 1 H, CH_aH_bCl), δ 1.28 (s, 15 H, (η^5-C_5Me_5)). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 108.5 (η^5-C_5Me_5), δ 42.9 (CH_2, $J_{CH} = 159$ Hz), δ 9.2 (η^5-C_5Me_5). IR (CH_2Cl_2): ν_{NO} 1775 cm^{-1}. MS (^{101}Ru): [M$^+$] *m/e* 350 (12%). Anal. Calcd for $C_{11}H_{17}NOCl_2Ru$: C, 37.62; H, 4.88; N, 3.99. Found: C, 38.01; H, 4.95; N, 3.78. Mp 148–155 °C dec.

Synthesis of Cp*Ru(NO)(CH_2Cl)$_2$. A mixture of Cp*Ru(NO)Cl_2 (0.05 g, 0.15 mmol), 2 g of Cu powder, and 40 mL of CH_2Cl_2 was vigorously stirred magnetically while ethereal diazomethane was added dropwise (ca. 1 mL/min) over 20 min. The reaction mixture was filtered through filter pulp into a clean Schlenk vessel containing 2 g of fresh Cu powder and a magnetic stir bar, and diazomethane addition was resumed for another 20 min. The reaction mixture was filtered into a clean Schlenk vessel and the solvent was removed in vacuo. The residue was extracted with 20 mL of 50 °C hexane, filtered through filter pulp, and concentrated to 5 mL. Crystallization at −40 °C gave 0.05 g (95%) of Cp*Ru(NO)(CH_2Cl)$_2$ as orange crystals. X-ray quality crystals were obtained by slow evaporation from hexane at 20 °C. Samples of Cp*Ru(NO)(CD_2Cl)$_2$ were prepared by substituting CH_2N_2 with CD_2N_2. ^{1}H NMR indicated ca. 70% deuteration as Cp*Ru(NO)(CD_2Cl)$_2$. ^{1}H NMR (C_6D_6): δ 4.32 (d, 2 H, CH_aH_bCl, $J_{ab} = 7.5$ Hz), δ 3.53 (d, 2 H, CH_aH_bCl), δ 1.40 (s, 15 H, η^5-C_5Me_5). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 105.7 (η^5-C_5Me_5), δ 43.5 (CH_2Cl, $J_{CH} = 145$ Hz), δ 9.4 (η^5-C_5Me_5). IR (CH_2Cl_2): ν_{NO} 1760 cm^{-1}. MS (^{101}Ru): [M$^+$] *m/e* 364 (19%). Anal. Calcd for $C_{12}H_{19}NOCl_2Ru$: C, 39.46; H, 5.24; N, 3.83. Found: C, 39.24; H, 4.99; N, 3.61. Mp 70–72 °C. Molar conductivity in CH_3NO_2 $\Lambda_M = 5.5$ (1) ohm^{-1} cm^2 mol^{-1}.

Photolysis Experiments. Solutions of Cp*Ru(NO)(CH_2Cl)Cl and Cp*Ru(NO)(CH_2Cl)$_2$ in C_6D_6 or $CDCl_3$ were prepared in 5-mm glass NMR tubes using 5–10 mg of complex and 0.75 mL of solvent and examined by ^{1}H NMR. The tubes were then placed vertically in a 100-mL beaker filled with water (maintained at 15 °C) and set directly next to a water-cooled medium-pressure Hanovia lamp for 5–10 min. Subsequent ^{1}H NMR analysis determined the effects of irradiation.

Infrared Examination of Gaseous Thermolysis Products. A 2 cm × 10 cm pathlength gas cell configured with a side-mounted 14/20 inner ground glass joint and 2 mm stopcock was used for the identification of gaseous products. The compounds were loaded as solutions into a 10 mL 14/20 flask containing finely divided glass fragments and dried under a stream of N_2. The system was carefully evacuated and then back-filled with N_2 in order to minimize sublimation of the compounds during the heating of the attached round-bottom flask. Typical sample sizes ranged between 0.005 and 0.01 g. The complexes were heated to 130 °C using a preheated oil bath. At this temperature the *bis*-chloromethyl complexes melted with visible gas evolution and eventually turned to a green solid within 5 min. The cell was then placed in the FT-IR instrument and a spectrum was obtained at 2-cm^{-1} resolution.

X-ray Structure of Cp*Ru(NO)(CH_2Cl)$_2$. A suitably sized crystal (0.06 × 0.12 × 0.20 mm^3) was mounted on a glass fiber with epoxy cement and centered on a Nicolet R3m/V diffractometer. Lattice parameters for a monoclinic cell were determined from 15 centered reflections in the range $16° < 2\theta < 24°$. The pattern of systematic absences was consistent with the space group $P2_1/n$. An empirical absorption correction was applied (ψ scan data, pseudoellipsoid model). The structure was solved by Patterson methods, and the remaining non-hydrogen atoms were located in subsequent difference Fourier difference maps. Hydrogen atoms were generated in idealized positions and given fixed (0.08) isotropic thermal parameters. The SHELXTL PLUS computational package was used throughout the solution and refinement process. The final cycles of least-squares refinement converged to $R = 5.50\%$, $R_w = 5.50\%$ for 1416 observed data ($F > 4\sigma F$) and 154 parameters.

X-ray Structure of Cp*Ru(NO)Et_2. The complex was prepared by published procedures[3c] and X-ray quality crystals were grown from hexane at −40 °C. A suitably sized specimen (0.10 mm × 0.20 mm × 0.20 mm) was fixed in a 0.3-mm thin-wall X-ray capillary with silicon grease and centered on a Siemens P4/Series II diffractometer (Mo Kα radiation) equipped with a low-temperature device set at 193 K. A primitive triclinic cell was chosen and θ–2θ data were collected in the range $3° < 2\theta < 45°$. The Ru atom was located by direct methods, and the remaining non-hydrogen atoms were located by subsequent least-squares cycles and difference maps. Anisotropic refinement (the hydrogens fixed in riding positions with isotropic (0.08) thermal parameters) converged to $R/R_w = 4.18\%/4.87\%$ with a data:parameter ratio of 10.6:1.

Acknowledgment. The support of the National Science Foundation for the J.L.H. research group (CHE-8901855) and the purchase of X-ray diffractometers (Vermont EPSCoR, R11-8601679; Utah State University, CHE-9002379) and the Utah State University Research Office are gratefully acknowledged. We acknowledge a generous loan of $RuCl_3 \cdot 3H_2O$ from Johnson-Matthey.

Registry No. Cp*Ru(NO)(CH_2Cl)Cl, 108419-16-5; Cp*Ru(NO)(CH_2Cl)$_2$, 136676-23-8; Cp*Ru(NO)Cl_2, 90419-99-1.

Supplementary Material Available: Tables giving details of the structure determination of Cp*Ru(NO)(CH_2Cl)$_2$, fractional atomic coordinates, equivalent isotropic displacement parameters, complete lists of bond lengths and bond angles, anisotropic displacement parameters, and H atom coordinates and complete details of the X-ray structure determination of Cp*Ru(NO)Et_2, including anisotropic thermal parameters, an ORTEP drawing, and a listing of calculated H atom positions (10 pages); tables of calculated and observed structure factors (17 pages). Ordering information is given on any current masthead page.

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