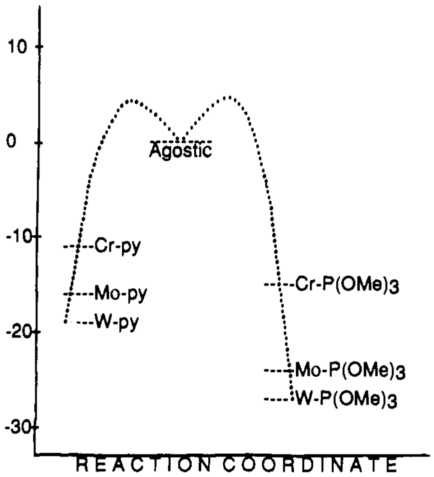

Figure 6. Potential energy diagram (enthalpy of reaction in kcal/mol) for reactions of $M(CO)_3(PCy_3)_2(py)$ with $P(OMe)_3$ (M = Cr, Mo, W). Enthalpies of activation are shown for W only, but values for Cr and Mo are similar, as shown in Table VIII.

Conclusion

It is well-known that the M–L bond lengths for low-valent complexes are in the order Cr < W = Mo and indeed were found to be 0.10–0.14 Å shorter in $Cr(CO)_3(PCy_3)_2$ compared to its W analogue. The consequences of pulling the ligands in along the metal axis will be to increase the effective "cone angle",[17] as illustrated in Figure 5. As a result, the steric environment facing an incoming ligand is more severe for the first-row metal. This is seen in faster rates of dissociation, slower rates of association, and lower than expected enthalpies of ligand binding for bulky ligands. In addition, larger ligand selectivities and different types of reactivity are also shown; however, these effects cannot be attributed to stark or sudden changes. It seems most likely that the chromium complex suffers an additional destabilization due to its smaller size and that this is on the order of 3–7 kcal/mol for bulky ligands. The experimental data reported here provide some of the first direct comparisons of these effects for a complete series of sterically crowded complexes. Additional thermodynamic and kinetic studies on these and related complexes are in progress.

Acknowledgment. Support of this work by National Science Foundation Grant CHE-8618753 is gratefully acknowledged. Special thanks are due to Dr. Nita Lewis and Mr. Daniel Taveras at the University of Miami for use of the stopped-flow equipment.

Supplementary Material Available: Tables giving additional data for the crystal structure of $Cr(CO)_3(P(C_6H_{11})_3)_2$, including atomic coordinates and equivalent isotopic displacement coefficients, bond lengths, bond angles, anisotropic displacement coefficients, and H atom coordinates and isotropic displacement coefficients (10 pages); tables of observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

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The Role of the 16-Electron $[(\eta^5\text{-}C_5Me_5)Ru(NO)]$ Transient in the Formation of Dinuclear Complexes and in Oxidative Addition Reactions

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Abstract: The formation of $[Cp^*Ru(\mu\text{-}NO)]_2$ (**2**) from the treatment of $Cp^*Ru(NO)Cl_2$ (**1**) with Zn dust in EtOH is preceded by the formation of an intermediate complex $[Cp^*Ru(\mu\text{-}NO)Cl]_2$ (**4**) containing a formal Ru–Ru single bond ($Cp^* = \eta^5\text{-}C_5Me_5$). Complex **4** is fully characterized, including a single-crystal X-ray structure: monoclinic space group $P2_1/n$, $a = 8.272$ (3) Å, $b = 14.722$ (5) Å, $c = 9.863$ (3) Å, $\beta = 107.42$ (2)°, $Z = 4$, $R_w = 5.28\%$, based on 1301 observed data ($F > 4.0\sigma(F)$). The structure shows a centrosymmetric trans geometry with bridging nitrosyl ligands, terminal chloride ligands, and a Ru–Ru distance of 2.684 (2) Å. Purified complex **4** reacts further with Zn dust in EtOH to give **2** quantitatively. Complex **4** is formed together with $Cp^*Ru(NO)(CH_2Cl)Cl$ (**6**) in the reaction of $Cp^*Ru(NO)Ph_2$ (**5a**) with CH_2Cl_2. The fact that complex **4** is formed in high yield from the thermolysis of an equimolar mixture of **5a** and **1** in ethanol suggests that any $[Cp^*Ru(NO)]$ transients produced in the Zn reaction are efficiently trapped to complex **4** by excess **1**. Crossover experiments involving **5a** and $Cp^*Ru(NO)(p\text{-tolyl})_2$ (**5b**) help verify that the generation of the 16-electron $[Cp^*Ru(NO)]$ species is the first process to occur when $Cp^*Ru(NO)(aryl)_2$ complexes are thermalized in chlorinated and non-chlorinated solvents. Thermolysis of **5a** in 1,2-dichloroethane gives complex **4** and ethylene, apparently through the generation of an unstable β-chloroethyl complex which decomposes to ethylene and dichloride complex **1**; the absence of **1** in the final reaction residue is attributed to its consumption by $[Cp^*Ru(NO)]$ transients, leading to **4** as the only observed organometallic product.

Introduction

Although certain 16-electron $(\eta^5\text{-}C_5R_5)ML$ species are known to activate C–H and C–halogen bonds,[2] their role in the formation and reactivity of the 32-electron $[(\eta^5\text{-}C_5R_5)M(\mu\text{-}L)]_2$ dimers (containing formal metal–metal double bonds) is less clear (R = H, CH_3; M = Rh, Ir; L = CO, PR_3, CNR).[3] Jones and Feher have reported the formation of $[Cp^*Rh(\mu\text{-}CNR)]_2$ complexes from the reduction of $Cp^*Rh(CNR)X_2$ precursors,[4] but have recently called into question the presence of a $[Cp^*Rh(CNR)]$ 16-electron transient, since no C–H activation is observed ($Cp^* = \eta^5\text{-}C_5Me_5$).[5]

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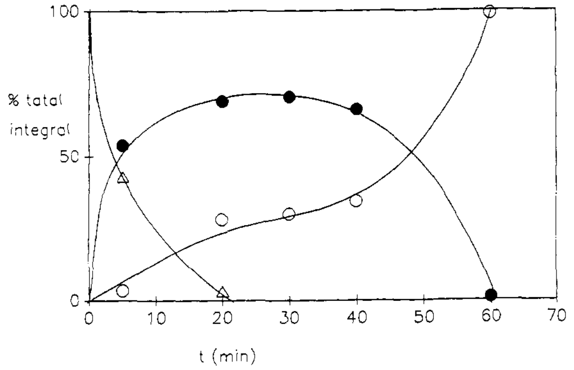

Figure 1. Profile of the reaction of complex **1** with Zn in EtOH, as monitored by ^{1}H NMR spectroscopy (△, δ 1.12; ●, δ 1.47; ○, δ 1.51).

Bergman and Chang recently reported the synthesis of $[Cp^*Ru(\mu\text{-}NO)]_2$ (**2**) by treating ethanolic solutions of $Cp^*Ru(NO)Cl_2$ (**1**) with Zn dust.[6] We have used a similar technique to form $[Cp^*Fe(\mu\text{-}NO)]_2$ from $Cp^*Fe(NO)Br_2$ in excellent yield.[7] While not known to activate C–H bonds, the transient $[Cp^*Ru(NO)]$ species generated by the thermolysis of $Cp^*Ru(NO)Ph_2$ was trapped by PMe_3 to give $Cp^*Ru(NO)PMe_3$. Furthermore, the $[Cp^*Ru(NO)]$ transient was shown to activate a C–Cl bond of CH_2Cl_2, and its role in the formation of the dinuclear byproducts $[Cp^*Ru(\mu\text{-}NO)]_2$ (**2**) and $[Cp^*Ru(\mu\text{-}NO)Ph]_2$ (**3a**) was postulated.[6]

Our interest in this area stems from our studies of the reactivity of the halomethyl complexes $(\eta^5\text{-}C_5R_5)Ru(NO)(CH_2X)X$ and $(\eta^5\text{-}C_5R_5)Ru(NO)(CH_2X)_2$ derived from the treatment of $(\eta^5\text{-}C_5R_5)Ru(NO)X_2$ precursors with diazomethane (R = H, Me; X = Cl, Br, I).[8] Our familiarity with the properties of $[(\eta^5\text{-}C_5H_5)Ru(\eta\text{-}NO)]_2$, as an excellent precursor to $(\eta^5\text{-}C_5H_5)Ru(NO)Br_2$,[9] caused us to be concerned with the anomalously high ν_{NO} frequency reported for complex **2**.[6] As a basis for comparison, the ν_{NO} of $[Cp^*Fe(\mu\text{-}NO)]_2$ is 30 cm^{-1} lower than the ν_{NO} of $[(\eta^5\text{-}C_5H_5)Fe(\mu\text{-}NO)]_2$.[10] The ν_{NO} frequency reported for **2** is 63 cm^{-1} ***higher*** than the ν_{NO} for $[(\eta^5\text{-}C_5H_5)Ru(\mu\text{-}NO)]_2$. A lower ν_{NO} for the Cp* derivative is generally observed upon replacement of the $\eta^5\text{-}C_5H_5$ ligand with the $\eta^5\text{-}C_5Me_5$ ligand and is attributed to the greater donor strength of the $\eta^5\text{-}C_5Me_5$ ligand.[11] We suspected that a less unsaturated dinuclear complex, perhaps generated from the partial reduction of complex **1**, might be responsible for the ν_{NO} at 1530 cm^{-1}.

Herein, we describe the reinvestigation of the reaction of **1** and Zn in EtOH, showing the formation of a dinuclear complex $[Cp^*Ru(\mu\text{-}NO)Cl]_2$ (**4**) to be intermediate between **1** and **2**. We also show that complex **4** is the dinuclear organometallic product from the thermal reaction of $Cp^*Ru(NO)Ph_2$ (**5a**) in the presence of chloroalkanes. Control experiments utilizing $Cp^*Ru(NO)(aryl)_2$ complexes have been carried out to more fully characterize the reductive elimination process that generates the $[Cp^*Ru(NO)]$ transient and the ability of the transient to undergo oxidative addition reactions with C–Cl, Ru–Ph, and Ru–Cl bonds.

Results and Discussion

Reductive Dimerization. Figure 1 shows a profile of the reaction of complex **1** with Zn dust in EtOH (eq 1) as monitored by the ^{1}H NMR singlets characteristic of the Cp* ligand in C_6D_6. The

$$\underset{\mathbf{1}}{Cp^*Ru(NO)Cl_2} + Zn \xrightarrow{EtOH} \underset{\mathbf{2}}{[Cp^*Ru(\mu\text{-}NO)]_2} \quad (1)$$

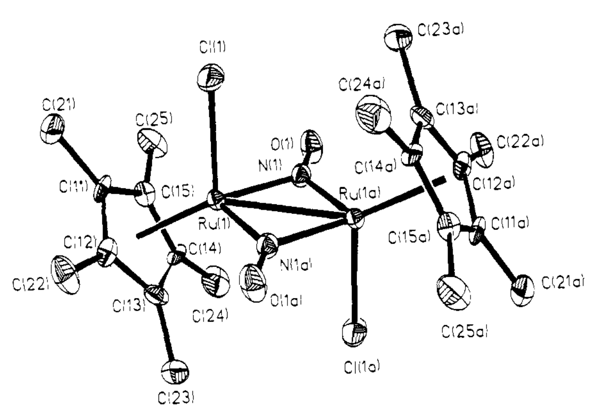

Figure 2. X-ray structure of Complex **4**.

Table I. Selected Geometric Data for Complex **4**

Bond Distances, Å			
Ru(1)–Cl(1)	2.409 (4)	Ru(1)–Ru(1a)	2.684 (2)
Ru(1)–N(1)	1.96 (1)	N(1)–O(1)	1.21 (1)
Ru(1)–N(1a)	1.932 (9)	Ru(1)–$Cp_{centroid}$	1.878
Bond Angles, deg			
Ru(1)–N(1)–O(1)	135.1 (8)	Cl(1)–Ru(1)–N(1)	89.9 (3)
Ru(1a)–N(1)–O(1)	137.6 (9)	Ru(1a)–Ru(1)–Cl(1)	93.2 (1)
N(1)–Ru(1)–N(1a)	92.8 (4)	$Cp_{centroid}$–Ru(1)–Ru(1a)	146.5
N(1)–Ru(1)–Ru(1a)	46.0 (3)		
Torsion Angles, deg			
$Cp_{centroid}$–Ru(1)–N(1)–O(1)	45.4		
$Cp_{centroid}$–Ru(1)–Ru(1a)–Cl(1a)	5.2		
Cl(1)–Ru(1)–N(1)–O(1)	82.4		

H NMR signal of **1** (δ 1.12) rapidly disappears as two new singlets at δ 1.47 and δ 1.51 appear. At 30 min reaction time, the signal at δ 1.12 is no longer detected and the δ 1.47 signal is nearly twice as large as the signal at δ 1.51. Qualitatively, the disappearance of the δ 1.47 singlet roughly matches the growth of the δ 1.51 signal. After 60 min, filtration of this reaction mixture through SiO_2 with CH_2Cl_2 and removal of solvent results in the isolation of a brick-red powder which we identify as $[Cp^*Ru(\mu\text{-}NO)]_2$ (**2**) (96% yield based on **1**). The ^{1}H NMR signal we observe at δ 1.51 in C_6D_6 for **2** is different from the δ 1.47 previously reported.[6] Besides having an elemental analysis and mass spectrum characteristic of complex **2**, the brick-red solid exhibits a single, strong ν_{NO} absorption at 1455 cm^{-1}. The value of ν_{NO} that we observe for complex **2** is 17 cm^{-1} lower than that reported for $[(\eta^5\text{-}C_5H_5)Ru(\mu\text{-}NO)]_2$,[9] and is consistent with the increased electron donating ability of the $\eta^5\text{-}C_5Me_5$ ligand.

If the reaction mixture described in eq 1 is quenched at 30 min by a quick filtration through SiO_2 with CH_2Cl_2, the resulting brownish-red residue displays IR and ^{1}H NMR signals characteristic of **2** together with an ^{1}H NMR signal at δ 1.47 in C_6D_6 and another strong IR absorption at 1530 cm^{-1}. Column chromatography of the reaction residue on SiO_2 with CH_2Cl_2 results in the clean separation of complex **2** from a slower moving brown zone. After removal of solvent, the brown zone yields a brown, microcrystalline material which we identify as $[Cp^*Ru(\mu\text{-}NO)Cl]_2$ (**4**) on the basis of elemental analysis, NMR and IR spectroscopy, mass spectrometry, and X-ray diffraction methods. The ^{1}H NMR and IR features of complex **4** correspond to the data previously reported for complex **2**.[6]

The X-ray structure of complex **4** is shown in Figure 2. Selected bond lengths and bond angles are provided in Table I. In the solid state, the complex adopts a crystallographically imposed centrosymmetric trans structure, with an inversion center located at the centroid of the Ru–Ru bond. The Ru(1)–Ru(1a) bond distance in **4** is 2.684 (2) Å, consistent with a formal Ru–Ru single bond, and intermediate between the rather short 2.614 (1) Å Ru–Ru separation found for $[\{Ru(acac)_2\}_2(\mu\text{-}NO)_2]$[12] and the

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somewhat longer $\mathrm{Ru_2}$ separations found for carbonyl or alkylidene-bridged structures.[13,14]

The data presented to this point clearly show complex **4** to be an intermediate toward the formation of **2** when complex **1** is treated with Zn dust (eq 2). ^{1}H NMR and IR spectroscopy provide no evidence for the existence of the cis isomer of complex **4**. Subsequent treatment of purified **4** with Zn dust results in

$$\underset{\mathbf{1}}{\mathrm{Cp^*Ru(NO)Cl_2}} \xrightarrow{\mathrm{EtOH/Zn}} \underset{\mathbf{4}}{[\mathrm{Cp^*Ru(\mu\text{-}NO)Cl}]_2} \xrightarrow{\mathrm{EtOH/Zn}} \underset{\mathbf{2}}{[\mathrm{Cp^*Ru(\mu\text{-}NO)}]_2} \tag{2}$$

essentially quantitative formation of complex **2** (eq 2). From the data in Figure 1, one can see that the Zn reduction of complex **4** is significantly slower than the reduction process that consumes complex **1**.

Reaction of Complexes 2 and 4 with $\mathrm{Cl_2}$ and Halocarbons. The stepwise addition of $\mathrm{Cl_2}$ to complex **2** can be observed by ^{1}H NMR spectroscopy. The treatment of complex **2** with substoichiometric amounts of $\mathrm{Cl_2}$ in $\mathrm{C_6D_6}$ results mostly in the formation of complex **1**, but smaller amounts of **4** (ca. 10% the amount of **1**) are consistently detectable by ^{1}H NMR (eq 3). The lower yield of **4**

$$\underset{\mathbf{2}}{[\mathrm{Cp^*Ru(\mu\text{-}NO)}]_2} + \tfrac{1}{2}\mathrm{Cl_2} \xrightarrow{\mathrm{C_6D_6}} \underset{\mathbf{1}}{\mathrm{Cp^*Ru(NO)Cl_2}} + \underset{\mathbf{4}}{[\mathrm{Cp^*Ru(\mu\text{-}NO)Cl}]_2} \tag{3}$$

may be a consequence of its faster reactivity with $\mathrm{Cl_2}$ as compared to complex **2**. As monitored by ^{1}H NMR spectroscopy in $\mathrm{C_6D_6}$, both **2** and **4** react with excess $\mathrm{Cl_2}$ to give **1** in virtually quantitative yield. The chlorination of **2** leading to the formation of *trans*-**4** can be compared to the formation of *trans*-1,2-dihalide products when halogens add to olefins.

Complex **2** reacts completely with $\mathrm{CDCl_3}$ in 24 h to give a nearly 1:1 mixture of **1** and **4** as observed by ^{1}H NMR spectroscopy. After 48 h, only complex **1** is observed. In $\mathrm{CH_2Cl_2}$ at 50 °C, complex **2** is relatively more stable, showing only 30% conversion to complex **4** and ca. 5% conversion to complex **1** after 16 h.

Crossover Experiments. Having isolated and characterized complex **4**, we now address the issue of its formation. The important question in the Zn reaction involves the differentiation between an odd-electron process involving a possible [Cp*Ru(NO)Cl] species and a process involving the coupling of 16-electron [Cp*Ru(NO)] transients. As mentioned earlier, there has been some concern that odd-electron intermediates may be involved in the reductive dimerization of $\mathrm{Cp^*Rh(CNR)X_2}$ complexes.[5] In an attempt to assess the possible role of the 16-electron [Cp*Ru(NO)] transient, we begin with a discussion of experiments designed to test for aryl crossover when the [Cp*Ru(NO)] transient is generated from thermolysis of $\mathrm{Cp^*Ru(NO)(aryl)_2}$ complexes.

The result of heating equimolar mixtures of diphenyl complex **5a** and $\mathrm{Cp^*Ru(NO)(p\text{-}tolyl)_2}$ (**5b**) in hexane is shown in eq 4.

$$\begin{aligned}&\underset{\mathbf{5a}}{\mathrm{Cp^*Ru(NO)Ph_2}} + \underset{\mathbf{5b}}{\mathrm{Cp^*Ru(NO)(\mathit{p}\text{-}tolyl)_2}} \xrightarrow{\text{hexane, 50 °C, 16 h}} \\ &\mathrm{Ph{-}Ph} + \text{tolyl–tolyl} + \mathbf{2} + \\ &\underset{\mathbf{3a}}{[\mathrm{Cp^*Ru(\mu\text{-}NO)Ph}]_2} + \underset{\mathbf{3b}}{[\mathrm{Cp^*Ru(\mu\text{-}NO)(\mathit{p}\text{-}tolyl)}]_2}\end{aligned} \tag{4}$$

The lack of any detectable *p*-phenyltoluene by ^{1}H NMR indicates the operation of an intramolecular reductive elimination step leading to biphenyl or *p,p'*-bitoluene and a [Cp*Ru(NO)] transient. This strongly supports the Bergman and Chang proposal that formation of $[\mathrm{Cp^*Ru(\mu\text{-}NO)Ph}]_2$ (**3a**) occurs via a formal insertion of a [Cp*Ru(NO)] transient into a Ru–phenyl bond of **5a** and the formation of complex **2** from the coupling of [Cp*Ru(NO)] transients.[6]

Heating equimolar amounts of complexes **5a** and **5b** in $\mathrm{CH_2Cl_2}$ (eq 5) gives a 3:1 mixture of complexes **4** and **6** and no evidence

$$\begin{aligned}&\mathbf{5a} + \mathbf{5b} \xrightarrow{\mathrm{CH_2Cl_2}\text{, 50 °C, 16 h}} \underset{\mathbf{4}\ (25\%)}{[\mathrm{Cp^*Ru(\mu\text{-}NO)Cl}]_2} + \\ &\underset{\mathbf{6}\ (75\%)}{\mathrm{Cp^*Ru(NO)(CH_2Cl)Cl}} + \mathrm{Ph{-}Ph} + \text{tolyl–tolyl}\end{aligned} \tag{5}$$

of complexes **3a** or **3b**. The fact that *p*-phenyltoluene and *p*-chlorotoluene are not formed indicates that reductive elimination to give a Ph–Ph or tolyl–tolyl bond is again the first step in the reaction and that no Cl abstraction occurs. Formation of $\mathrm{Cp^*Ru(NO)(CH_2Cl)Cl}$ (**6**) is therefore consistent with an oxidative addition of $\mathrm{CH_2Cl_2}$ to the [Cp*Ru(NO)] transient. The large excess of $\mathrm{CH_2Cl_2}$ present apparently precludes the formation of **3a** or **3b**. The formation of complex **4** in eq 5 can be explained by the thermal instability of complex **6** (to give **1** and polymethylene[8]) together with the results of the reaction shown in eq 6. Here we show that the thermolysis of an equimolar mixture

$$\underset{\mathbf{1}}{\mathrm{Cp^*Ru(NO)Cl_2}} + \underset{\mathbf{5a}}{\mathrm{Cp^*Ru(NO)Ph_2}} \xrightarrow{\text{EtOH, 50 °C}} \underset{\mathbf{4}}{[\mathrm{Cp^*Ru(\mu\text{-}NO)Cl}]_2} \tag{6}$$

of complexes **1** and **5a** in EtOH affords exclusively **4** in 92% isolated yield. Thus, any amount of **1** produced from the thermal decomposition of **6** is likely trapped by the [Cp*Ru(NO)] transient present in the reaction mixture, leading to the formation of complex **4**. The complete absence of complex **2** in eqs 5 and 6 shows that the [Cp*Ru(NO)] transient is so efficiently trapped by either $\mathrm{CH_2Cl_2}$ or complex **1** that the dimerization to give complex **2** is not observed.

Reaction of Complex 5a with 1,2-Dichloroethane. A solution of complex **5a** in $\mathrm{C_6D_6}$ reacts with excess 1,2-dichloroethane to give complex **4** and ethylene (eq 7). Ethylene evolution is consistent with the oxidative addition of 1,2-dichloroethane to the [Cp*Ru(NO)] transient, giving an unstable β-chloroethyl complex which rapidly eliminates ethylene (eq 8). The absence of complex **1** in eq 7 is again consistent with it being trapped by the [Cp*Ru(NO)] transient, leading exclusively to the formation of **4** (eq 8).

$$\underset{\mathbf{5a}}{\mathrm{Cp^*Ru(NO)Ph_2}} + \mathrm{ClCH_2CH_2Cl} \xrightarrow{\mathrm{C_6D_6}\text{, 50 °C}} \mathrm{CH_2{=}CH_2} + \underset{\mathbf{4}}{[\mathrm{Cp^*Ru(\mu\text{-}NO)Cl}]_2} + \mathrm{Ph{-}Ph} \tag{7}$$

$$\begin{array}{ccc}\underset{\text{(unstable)}}{[\mathrm{Cp^*(NO)(Cl)RuCH_2CH_2Cl}]} & \longrightarrow & \underset{\mathbf{1}}{\mathrm{Cp^*Ru(NO)Cl_2}} + \mathrm{CH_2{=}CH_2} \\ & & \Big\downarrow{\scriptstyle +[\mathrm{Cp^*Ru(NO)}]} \\ & & \mathbf{4}\end{array} \tag{8}$$

Conclusions. The formation of complex **2**, which contains a formal Ru=Ru double bond, has been shown to occur by two different pathways. The reaction giving complex **4** during Zn reduction of dihalide complex **1** is an intermediate step toward the formation of the dimer complex **2**. The conversion of complex **4** to complex **2** by Zn is independent of the reduction of complex **1** and may likely involve an odd-electron process. From previous[6] and present investigations of the thermolysis of $\mathrm{Cp^*Ru(NO)(aryl)_2}$ complexes, it is apparent that formation of complex **2** is also consistent with [Cp*Ru(NO)] dimerization under conditions where the transient is not rapidly trapped by C–Cl, Ru–Ph, or Ru–Cl bonds.

It is not possible to completely rule out the role of a 17-electron [Cp*Ru(NO)Cl] dimerization process leading to complex **4** when complex **1** is treated with Zn. However, the fact that complex **1** so efficiently traps the 16-electron [Cp*Ru(NO)] transient coupled with the fact that complex **4** is the major product early

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in the Zn reaction suggests that [Cp*Ru(NO)] transients are generated and rapidly trapped to complex **4** in the reaction of **1** with Zn.

Experimental Section

Standard Schlenk techniques were employed in all syntheses. The nitrogen reaction atmosphere was purified by passage through scavengers for water (Aquasorb, Mallinckrodt) and oxygen (Catalyst R3-11, Chemical Dynamics, So. Plainfield, NJ). The column chromatography support used was SiO_2 (60–200 mesh, Baker) activated by drying under a 1×10^{-5} Torr vacuum for 24 h. CH_2Cl_2 and 1,2-dichloroethane were distilled from CaH_2 and acetone was distilled from molecular sieves prior to use. Anhydrous methanol and ethanol (J. T. Baker) were saturated with N_2 before use. $RuCl_3 \cdot nH_2O$ (n = 2–3) was obtained as a gift from Johnson Matthey and reagent grade Zn dust was used as received from Baker. Pentamethylcyclopentadiene[15] and Cp*Ru(NO)Ph_2[6] were prepared by literature methods. We report here a new, more efficient synthetic route to Cp*Ru(NO)Cl_2 from $[Cp^*RuCl_2]_x$[16] and nitric oxide (C.P. grade, Linde). Infrared spectra were recorded on a Mattson Polaris-Icon FT spectrophotometer. The ^1H and ^{13}C NMR spectra were recorded on a Varian XL 300 spectrometer at 300 and 75.4 MHz, respectively. Residual solvent peaks were used as internal standards (7.15 ppm [^1H] and 128.0 ppm [^{13}C] for C_6H_6; δ 7.24 [^1H] for $CDCl_3$). Mass spectra were obtained with a LKB 2091 mass spectrometer using electron impact ionization and a heated direct inlet probe. Melting points were measured with a mel-temp device (Laboratory Devices) in sealed capillaries and are uncorrected. Combustion analyses were performed by Robertson Laboratories, Inc., Madison, NJ.

Synthesis of Cp*Ru(NO)Cl_2 (1). Following the literature preparation for $[Cp^*RuCl_2]_x$,[16] 1.31 g of $RuCl_3 \cdot 3H_2O$ (5.0 mmol) was dissolved in 30 mL of methanol and 1.22 g of C_5Me_5H (8.9 mmol) was added. The solution was heated at reflux for 3 h and then cooled at −40 °C for 1 h. The methanol was decanted away and the resulting red-brown crystals were washed three times with hexane (20 mL). The crystals were dissolved in 30 mL of CH_2Cl_2 and NO(g) was bubbled directly through the solution for 10 min. A color change from reddish-brown to dark green was observed. The solution volume was then reduced in vacuo to 10 mL and transferred to a 3 × 10 cm column of SiO_2 prepared in CH_2Cl_2. Elution with a 95/5 (v/v) mixture of CH_2Cl_2/acetone produced a green zone which, after removal of solvent, gave 1.14 g (3.4 mmol, 68% yield) of Cp*Ru(NO)Cl_2 (**1**) as a green, microcrystalline powder. ^1H NMR (C_6D_6) δ 1.12, ($CDCl_3$) δ 1.84. Other spectral and analytical data were in agreement with those previously reported.[17]

Reaction Profile of Complex 1 with Zn in EtOH. A Schlenk flask was charged with complex **1** (0.10 g, 0.3 mmol), 0.5 g (7.6 mmol) of Zn powder, and a stir bar and capped with a septum. The vessel was subjected to several pump/N_2-refill cycles and 20 mL of N_2 saturated EtOH was added via syringe. The reaction mixture was stirred vigorously at room temperature, and 1-mL aliquots were removed at 5, 20, 30, 40, 60, and 80 min from the time of EtOH addition. Each aliquot was immediately taken to dryness, extracted with 1.0 mL of C_6D_6, and examined by ^1H NMR to determine the reaction composition.

Preparation of $[Cp^*Ru(\mu\text{-}NO)Cl]_2$ (4). A preparative-scale reaction followed the above procedure using 0.50 g (1.5 mmol) of **1**, 50 mL of EtOH, and 1.5 g (23 mmol) of Zn powder. Twenty-five minutes after the addition of EtOH, the reaction mixture was quickly filtered through a 3 × 5 cm plug of SiO_2 with CH_2Cl_2 and taken to dryness in vacuo. The residue was redissolved in 10 mL of CH_2Cl_2 and carefully transferred to the top of a 2.5 × 35 cm column of SiO_2 prepared in CH_2Cl_2. Elution with CH_2Cl_2 produced a well-resolved red zone, which after removal of solvent in vacuo gave 0.090 g (0.17 mmol, 22% yield) of **2**: ^1H NMR (C_6D_6) δ 1.51 (s, Cp*), ($CDCl_3$) δ 1.63 (s); $^{13}C\{^1H\}$ (C_6D_6) δ 8.40 (η^5-C_5Me_5), δ 97.14 (η^5-C_5Me_5); IR (KBr) ν_{NO} 1455 cm^{-1} (vs); combustion analysis and mass spectral data matched those previously reported.[6]

Further elution of the column with 95/5 CH_2Cl_2/acetone produced a brown zone, which after removal of solvent gave 0.34 g (0.56 mmol, 75% yield) of **4** as a brown, microcrystalline solid. Crystals for X-ray and chemical analysis were grown by slow evaporation from a 2:1 CH_2Cl_2/hexane solution. Anal. Calcd for $C_{20}H_{30}N_2O_2Cl_2Ru_2$ (603.5): C, 39.80; H, 5.01; N, 4.64. Found: C, 39.92; H, 5.13; N, 4.68. No detectable melting point below 200 °C; IR (KBr) ν_{NO} 1530 cm^{-1} (vs), (CH_2Cl_2) ν_{NO} 1537 cm^{-1}; ^1H NMR (C_6D_6) δ 1.47 (s), ($CDCl_3$) δ 1.65 (s); $^{13}C\{^1H\}$ (CD_2Cl_2) δ 9.36 (η^5-C_5Me_5), δ 106.4 (η^5-C_5Me_5); MS (EI) [M^+] m/e 603 (5%), [M − Cl] m/e 568 (17%), [M − Cl_2] m/e 533 (53%), [M/2] m/e 302 (100%).

Alternate Synthesis of Complex 4. A Schlenk flask was charged with complex **5a** (0.05 g, 0.12 mmol), complex **1** (0.04 g, 0.12 mmol), and a stir bar. Ethanol (7 mL) was added and the vessel was evacuated. After the vessel was heated in a 50 °C oil bath for 16 h it was cooled to room temperature. Complex **4** was isolated as lustrous, dark brown crystals after the reaction solvent was decanted and washed once with hexane (0.066 g, 0.11 mmol, 92% yield).

Reaction of 4 with Zn Powder. A Schlenk flask was charged with 0.10 g (0.17 mmol) of **4**, 0.25 g (3.8 mmol) of Zn powder, 20 mL of EtOH, and a magnetic stir bar. After being vigorously stirred for 1.5 h, the reaction mixture was filtered through a 3 × 5 cm plug of SiO_2 with CH_2Cl_2 and taken to dryness in vacuo, yielding 0.086 g (0.16 mmol, 98% yield) of **2**.

Reaction of Cp*Ru(NO)Ph_2 (5a) with CH_2Cl_2. A solution of **5a** (0.10 g, 0.24 mmol) in CH_2Cl_2 (20 mL) was heated to 50 °C in an evacuated Schlenk flask for 18 h. ^1H NMR examination of the reaction mixture after removal of the CH_2Cl_2 showed a 1:3 mixture of **4** and Cp*Ru(NO)(CH_2Cl)Cl (**6**). Chromatography of the mixture on a 1 × 10 cm SiO_2 column with CH_2Cl_2 resulted in the elution of **4** (0.035 g, 48% yield). Complex **6** does not survive chromatography on SiO_2 under these conditions.[8]

Reaction of Complex 5a with 1,2-Dichloroethane. A 5-mm NMR tube was charged with **5a** (0.002 g), 10 μL of 1,2-dichloroethane, and ca. 0.7 mL of C_6D_6 (0.03% TMS added) and capped with a septum. After a starting spectrum was measured, the tube was heated to 50 °C. After 90 min the ^1H NMR spectrum showed ca. 10% of the starting complex **5a**, a new peak at δ 5.24 corresponding to ethylene and a peak at δ 1.47 which corresponded to complex **4**.

In a preparative reaction, complex **5a** (0.10 g, 0.24 mmol) was dissolved in 2 mL of 1,2-dichloroethane and heated for 90 min at 50 °C. The reaction mixture was transferred directly to a 1 × 10 cm SiO_2 column prepared in CH_2Cl_2; elution with CH_2Cl_2 produced a slow-moving brown zone, which after removal of solvent gave 0.045 g (63% yield) of complex **4**.

Characterization of Cp*Ru(NO)(p-tolyl)$_2$ (5b) and $[Cp^*Ru(\mu\text{-}NO)(p\text{-tolyl})]_2$ (3b). Preparation of **5b** and **3b** followed the general procedure for the syntheses of **5a** and **3a**,[6] using (p-tolyl)magnesium chloride in place of phenylmagnesium chloride (70–75% yield). **5b**: ^1H NMR (C_6D_6) δ 1.40 (s, 15 H, C_5Me_5); δ 2.24 (s, 6 H, C_6H_4-CH_3); δ 7.04 (d, 4 H), δ 7.42 (d, 4 H) (C_6H_4-CH_3); IR (KBr) ν_{NO} 1736 cm^{-1} (vs). **3b**: ^1H NMR (C_6D_6) δ 1.46 (s, 30 H, C_5Me_5); δ 2.12 (s, 6 H, C_6H_4-CH_3); δ 6.61 (d, 4 H), δ 6.68 (d, 4 H) (C_6H_4-CH_3); IR (KBr) ν_{NO} 1501 cm^{-1}.

Crossover Reaction of 5a and 5b in Hexane. A 50-mL vacuum bulb was charged with 0.043 g (0.10 mmol) of complex **5b**, 0.048 g (0.11 mmol) of complex **5a**, and 7 mL of hexane. The bulb was evacuated and heated in an oil bath for 16 h at 50 °C. The hexane was removed in vacuo and the residue examined by ^1H NMR spectroscopy in C_6D_6. The signals of complex **3a** and **3b** were present as well as aromatic signals due to biphenyl and the methyl groups of p,p'-bitoluene (δ 2.15). A signal characteristic of the methyl group of p-phenyltoluene (at δ 2.07) was not present. A small amount of tetramethylfulvene [δ 1.68 (s, 6 H), δ 1.85 (s, 6 H), and δ 5.33 (s, 2 H)] was also detected.

X-ray Analysis of 4. A suitable crystal was selected and mounted vertically on a glass fiber with epoxy cement. The crystal was optically centered on a Nicolet R3m/V diffractometer utilizing graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and a rotation photograph was taken. The auto-centering and indexing of 25 reflections indicated a primitive monoclinic cell. An axial photograph confirmed the presence of symmetry along the unique b axis. Systematic absences in the data set indicated the space group $P2_1/n$, an alternate setting of $P2_1/c$. The structure solution (by direct methods) and subsequent anisotropic refinement of non-hydrogen atoms utilized the SHELXTL PLUS package of programs. Hydrogen atoms were generated in idealized positions with fixed thermal parameters (0.08). The least-squares refinement converged at a final R = 7.21%, R_w = 5.28% for 1301 observed data ($F > 4\sigma F$) and 128 parameters.

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Registry No. 1, 90419-99-1; **2**, 108419-15-4; **3b**, 136660-30-5; **4**, 136660-28-1; **5a**, 108451-71-4; **5b**, 136660-29-2; **6**, 108419-16-5; C_5Me_5H, 41539-64-4; $RuCl_3$, 10049-08-8; CH_2Cl_2, 75-09-2; [(η^5-

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$C_5Me_5)Ru(NO)]$, 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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