C−(Halide) Oxidative Addition Routes to Ruthenium Carbenes

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$Ru(H)_2(H_2)_2L_2$ (L = PCy_3) reacts with $CHRCl_2$ (R = H, Ph) to give $Ru(CHR)Cl_2L_2$ and H_2. Using $Cl_2C{=}CH_2$ as the *gem*-dihalide gives $Ru(CHCH_3)Cl_2L_2$, due to hydrogenation of the C=C bond of the presumed vinylidene primary product by released H_2. Released H_2 also reacts with $Ru(CHR)Cl_2L_2$ (R = H, Ph) to give H_3CR, HCl and $RuHCl(H_2)L_2$. This undesirability of H_2 as a coproduct can be diminished by using $Ru(H)_2(N_2)_2L_2$ as the reagent, giving $Ru(CHR)Cl_2L_2$ and $1H_2$ and $2N_2$ as products. Reaction of $Ru(H)_2(N_2)_2L_2$ with Cl_2CHEt gives $RuCl_2(CHEt)L_2$ and $RuHCl(N_2)L_2$, the latter apparently by competitive β-H migration from an intermediate $RuHCl(CHClEt)L_2$ species. When $Ru(H)_2(N_2)_2L_2$ is reacted with the *monochloride* $PhCH_2Cl$, the primary product $RuCl(CH_2Ph)(H_2)L_2$ slowly (hours) evolves further to give $RuHCl(N_2)L_2$ and $PhCH_3$. Reaction of $Ru(H)_2(N_2)_2L_2$ with C_6F_6, BrHC=CHPh, and CH_3I give $RuHX(N_2)L_2$ (X = F, Br, I, respectively). The N_2 ligand in $RuHCl(N_2)L_2$ can be displaced by H_2 and by CO, while H_2 converts $RuHF(N_2)L_2$ to $Ru(H)_2(H_2)_2L_2$ and HF.

Introduction

Synthetic routes to nonheteroatom-stabilized carbene ligands are relatively limited in type; new approaches would not be unwelcome. The present state of the art has been reviewed.[1] Geminal dihalide compounds $RR'CX_2$ represent an attractive potential route,[2] by oxidative addition (eq 1), especially if the

$$L_nM + RR'CX_2 \xrightarrow{?} L_nX_2M{=}CRR' \qquad (1)$$

halide ligands in the product complex are subsequently used to introduce additional functionality (e.g., hydride, halide, alkoxide). Since two available C−X bonds react, eq 1 is likely to be a two-step process and might go wrong at the $L_nXM{-}CRR'X$ stage; α-halo alkyl complexes are known to be very susceptible to nucleophilic attack at C_α,[3] and migration of a β-H (within R or R′) to M could also occur. The oxidative addition of two C−X bonds to one M also represents a four-electron oxidation, which few metals are prepared to endure. The electron count of M increases by four during eq 1, which indicates that L_nM must be no more than a 14-valence electron species; this is rarely available. Finally, several halides on a single carbon can encourage electron transfer (eq 2), and the resulting radical anion

$$L_nM + RR'CX_2 \rightarrow L_nM^{\bullet+} + RR'CX_2^{\bullet-} \qquad (2)$$

can fail to accomplish the desired oxidative addition of C and X to M; it will therefore be necessary to avoid L_nM being too electron-rich and too easily oxidized by single-electron transfer. A rich source of successful examples is the reaction of an iminium salt with unsaturated or electron-rich metal complexes.[4] One example involves Ir(I) containing a good leaving group (eq 3).

$$IrCl(PPh_3)_2(N_2) + [CHNMe_2Cl]Cl \rightarrow IrCl_3(PPh_3)_2[C(H)(NMe_2)] \qquad (3)$$

We report here our results toward the above goal, which accomplishes the objective in part by *not* using a highly reduced metal, but instead relying on an (oxidatively induced) reductive elimination (of two hydrides, as H_2) to generate the needed reduced metal at a later stage of reaction than would make it vulnerable to eq 2. Part of this work has been reported in a preliminary communication.[5] Simultaneous with our initial report of *gem*-dihalides as sources of $RuCl_2(CHR)L_2$ species was a related report,[6] which differed primarily in the ruthenium source employed. While this paper was in review, another related route was reported, motivated by the utility of $Ru(CRR')Cl_2L_2$ complexes as olefin metathesis catalysts.[7]

Experimental Section

General. All reactions and manipulations were conducted using standard Schlenk and glovebox techniques under prepurified argon or nitrogen. Solvents were dried and distilled under argon, and stored in airtight solvent bulbs with Teflon closures. All NMR solvents were dried, vacuum-transferred, and stored in a glovebox. Vinylidene chloride, α,α-dichlorotoluene, 1,1-dichloropropane, and benzyl chloride were purchased from Aldrich and used after degassing. Gaseous reagents (H_2, N_2) were purchased from Air Products and used as received. $Ru(H)_2(H_2)_2(PCy_3)_2$[8] and $Ru(H)_2(N_2)_2(PCy_3)_2$[9] were prepared

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as reported. ^{1}H, ^{13}C{^{1}H} and ^{31}P NMR spectra were obtained on a Varian Gemini 300, while ^{2}H NMR spectra were recorded on a Varian Inova 400 instrument. Chemical shifts are referenced to residual solvent peaks (^{1}H, ^{2}H, ^{13}C{^{1}H}), or external H_3PO_4 (^{31}P). Infrared spectra were recorded on a Nicolet 510P FT-IR spectrometer.

Preparation of $RuCl_2(=CH_2)(PCy_3)_2$ from $Ru(H)_2(H_2)_2(PCy_3)_2$. Method A. To a suspension of $Ru(H)_2(H_2)_2(PCy_3)_2$ (100 mg, 0.15 mmol) in pentane (7 mL) was added CH_2Cl_2 (38 μL, 0.60 mmol) via syringe. The resulting suspension was stirred under argon at room temperature for 3 h. During this time, the color of the suspension changed from white to brown-red. The red solid obtained by filtration was washed with pentane and dried in vacuo. Yield: 70 mg (63%).

Method B. The reaction could also be carried out heating at 60 °C for 15 min, starting from $Ru(H)_2(H_2)_2(PCy_3)_2$ (100 mg, 0.15 mmol) and CH_2Cl_2 (14.4 μL, 0.22 mmol) in pentane (5 mL). Yield: 75 mg (67%). All the spectroscopic data are consistent with those reported previously.[10] When the crude suspension was dried in vacuo and dissolved in benzene-d_6, ^{1}H and ^{31}P NMR show the presence of $RuHCl(H_2)(PCy_3)_2$ (yield <15%) in addition to $RuCl_2(=CH_2)(PCy_3)_2$. This monochloride was shown independently to be formed by the action of H_2 on $RuCl_2(=CH_2)(PCy_3)_2$ (vide infra).

Preparation of $RuCl_2(=CD_2)(PCy_3)_2$ from $Ru(H)_2(H_2)_2(PCy_3)_2$. This compound was prepared analogously as described for $RuCl_2(=CH_2)(PCy_3)_2$ (Method A) by starting from $Ru(H)_2(H_2)_2(PCy_3)_2$ (50 mg, 0.075 mmol) and CD_2Cl_2 (19 μL, 0.30 mmol). ^{2}H NMR (61 MHz, C_6H_6): δ 19.4 (s, Ru=CD_2).

Preparation of $RuCl_2(=CH_2)(PCy_3)_2$ from $Ru(H)_2(N_2)_2(PCy_3)_2$. A solution of $Ru(H)_2(N_2)_2(PCy_3)_2$ (107.5 mg, 0.15 mmol) was prepared in situ by bubbling N_2 through a suspension of $Ru(H)_2(H_2)_2(PCy_3)_2$ (100 mg, 0.15 mmol) in pentane (15 mL) for 15 min (shorter bubbling times resulted in mixtures of $Ru(H)_2(H_2)_2(PCy_3)_2$, $Ru(H)_2(H_2)(N_2)(PCy_3)_2$, and $Ru(H)_2(N_2)_2(PCy_3)_2$. We have found that complete conversion to the bis-dinitrogen compound strongly depends on the flow rate of nitrogen. For this reason, it is highly advisable to ascertain complete conversion to $Ru(H)_2(N_2)_2(PCy_3)_2$ by ^{31}P NMR spectroscopy prior to any further reaction). To this *freshly* prepared solution of $Ru(H)_2(N_2)_2(PCy_3)_2$ was added CH_2Cl_2 (38 μL, 0.60 mmol) via syringe. After stirring at room temperature for 20 min, a brown-red suspension was obtained. The red solid obtained by filtration was washed with pentane and dried in vacuo; yield 78 mg (70%).

Spectroscopic Data for $Ru(H)_2(H_2)(N_2)(PCy_3)_2$. ^{1}H NMR: δ −8.48 (br s, 4H, $Ru(H)_2(H_2)$), 1.22−2.10 (m, 66H, PCy_3). ^{31}P{^{1}H} NMR: δ 69.6 (s).

Spectroscopic Data for $Ru(H)_2(N_2)_2(PCy_3)_2$. ^{1}H NMR is consistent with that reported previously.[9] ^{31}P{^{1}H} NMR: δ 60.1 (s).

Reaction of $RuCl_2(=CH_2)(PCy_3)_2$ with H_2. A solution of $RuCl_2(=CH_2)(PCy_3)_2$ (10 mg, 0.013 mmol) in benzene-d_6 (0.5 mL) was placed in an NMR tube with a Teflon closure. The solution was frozen in liquid N_2, the headspace was evacuated, and it was filled with H_2 (1 atm). Monitoring the reaction by ^{1}H and ^{31}P{^{1}H} NMR spectroscopies showed a clean conversion to $RuHCl(H_2)(PCy_3)_2$[11,12] within 18 h at 24 °C. In the ^{1}H NMR, a sharp singlet at 0.13 ppm was also observed, assigned, by comparison with a pure sample, to methane. This identification as CH_4 was also confirmed by evacuating the H_2 atmosphere of the tube and refilling it with CH_4. The ^{1}H NMR spectrum shows growth of the singlet at 0.13 ppm.

Reaction of $RuCl_2(=CH_2)(PCy_3)_2$ with H_2 in the Presence of NEt_3. The reaction was performed similarly as the one described above, but Et_3N (3.7 μL, 0.027 mmol) was added to the solution. After 18 h, a cloudy solution was obtained, and ^{31}P{^{1}H} and ^{1}H NMR spectroscopies showed conversion to $RuHCl(H_2)(PCy_3)_2$ and CH_4. [$HNEt_3$]Cl was observed as a cloudy white precipitate.

Reaction of $RuCl_2(=CH_2)(PCy_3)_2$ with H_2 in the Presence of $Ru(H)_2(H_2)_2(PCy_3)_2$. An equimolar solution of $RuCl_2(=CH_2)(PCy_3)_2$ (10 mg, 0.013 mmol) and $Ru(H)_2(H_2)_2(PCy_3)_2$ (8.9 mg, 0.013 mmol) in C_6D_6 (0.5 mL) was placed in an NMR tube. The solution was frozen in liquid N_2, the headspace was evacuated, and it was filled with H_2 (1 atm). Monitoring the reaction by ^{1}H and ^{31}P{^{1}H} NMR spectroscopies showed a clean conversion to $RuHCl(H_2)(PCy_3)_2$ within 18 h.

Reaction of $Ru(H)_2(H_2)_2(PCy_3)_2$ with HCl. A solution of $Ru(H)_2(H_2)_2(PCy_3)_2$ (10 mg, 0.015 mmol) in C_6D_6 (0.5 mL) was placed in an NMR tube with a Teflon closure. The solution was frozen in liquid N_2, the headspace was evacuated, and HCl (0.015 mmol) was condensed into the tube using a calibrated gas manifold. When the solution warmed to room temperature and the tube was shaken, immediate gas evolution was observed, together with a color change from beige to orange. ^{1}H and ^{31}P{^{1}H} NMR spectroscopies show clean conversion to $RuHCl(H_2)(PCy_3)_2$.

Preparation of $RuCl_2(=CHCH_3)(PCy_3)_2$ from $Ru(H)_2(H_2)_2(PCy_3)_2$. To a suspension of $Ru(H)_2(H_2)_2(PCy_3)_2$ (100 mg, 0.15 mmol) in pentane (7 mL) was added $Cl_2C=CH_2$ (36 μL, 0.45 mmol) via syringe. Immediately a brown-red solution was obtained from which a purple solid precipitated within 2 min. The purple solid obtained by filtration was washed with pentane and dried in vacuo. Yield 80 mg (70%).

From $Ru(H)_2(N_2)_2(PCy_3)_2$. This reaction was carried out in a similar way to that described for $RuCl_2(=CH_2)(PCy_3)_2$, starting from a *freshly* prepared solution of $Ru(H)_2(N_2)_2(PCy_3)_2$ (107.5 mg, 0.15 mmol) and $Cl_2C=CH_2$. Yield 80 mg (70%). This reaction was quantitative by NMR spectroscopies using a ratio $Ru/Cl_2C=CH_2$ of 1:1. All the NMR data are consistent with those reported previously.[10]

Reaction of $Ru(H)_2(H_2)_2(PCy_3)_2$ with $Cl_2C=CH_2$ in an NMR Tube. To a solution of $Ru(H)_2(H_2)_2(PCy_3)_2$ (8.4 mg, 0.0126 mmol) in C_6D_6 (0.5 mL) was added $Cl_2C=CH_2$ (1 μL, 0.0126 mmol) via syringe. The reaction was monitored by ^{1}H and ^{31}P{^{1}H} NMR spectroscopies. ^{1}H and ^{31}P{^{1}H} NMR spectra recorded after 5 min showed clean conversion to $RuCl_2(=CHCH_3)(PCy_3)_2$. ^{1}H and ^{31}P{^{1}H} NMR spectra recorded after 5 h show a mixture of $RuCl_2(=CHCH_3)(PCy_3)_2$ (75%) and $Ru(H)_2Cl_2(PCy_3)_2$ (25%); in the ^{1}H NMR spectrum there is also a singlet at 0.77 ppm, assigned (by comparison with a pure sample) to ethane. Spectroscopic data for $Ru(H)_2Cl_2(PCy_3)_2$:[14] ^{1}H NMR (300 MHz, C_6D_6, 20 °C): δ −11.93 (t, J_{P-H} = 32.1 Hz, 2H, Ru−H), 1.20−2.10 (m, 66H, PCy_3). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6, 20 °C): δ 89.9 (s).

Reaction of $Ru(H)_2(N_2)_2(PCy_3)_2$ with Cl_2CHPh. To a solution of $Ru(H)_2(N_2)_2(PCy_3)_2$ (11.2 mg, 0.0156 mmol) in C_6D_6 (0.5 mL) was added Cl_2CHPh (2 μL, 0.0156 mmol) via syringe. ^{1}H and ^{31}P{^{1}H} NMR spectra recorded after 5 min of reaction showed a mixture of $RuCl_2(=CHPh)(PCy_3)_2$[10] (65%), $RuH_2Cl_2(PCy_3)_2$ (7%) and $RuHCl(H_2)(PCy_3)_2$ (28%).

Reaction of $Ru(H)_2(N_2)_2(PCy_3)_2$ with $Cl_2CHCH_2CH_3$. To a solution of $Ru(H)_2(N_2)_2(PCy_3)_2$ (14.4 mg, 0.02 mmol) in C_6D_6 (0.5 mL) was added $Cl_2CHCH_2CH_3$ (2 μL, 0.02 mmol) via syringe. The reaction was monitored by ^{1}H and ^{31}P{^{1}H} NMR spectroscopies. After 10 min of reaction ^{1}H and ^{31}P{^{1}H} NMR spectroscopies revealed a mixture of unreacted $Ru(H)_2(N_2)_2(PCy_3)_2$, $RuCl_2(=CHCH_2CH_3)(PCy_3)_2$[10] and $RuHCl(N_2)(PCy_3)_2$ (vide infra). After 20 h, $RuHCl(N_2)(PCy_3)_2$ is the only Ru-containing compound present in the solution. 1-Chloropropane was detected by ^{1}H NMR spectroscopy upon vacuum transfer of the volatiles to another NMR tube.

Reaction of $Ru(H)_2(N_2)_2(PCy_3)_2$ with $PhCH_2Cl$: Formation of $RuHCl(N_2)(PCy_3)_2$. To a solution of $Ru(H)_2(N_2)_2(PCy_3)_2$ (12.5 mg, 0.017 mmol) placed in an NMR tube, $PhCH_2Cl$ (2 μL, 0.017 mmol) was added via syringe, causing an immediate color change from

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yellowish to red. After 10 min of reaction, the ^{1}H and ^{31}P{^{1}H} NMR spectra show a mixture of starting material (70%) and signals corresponding to a new species (30%) $RuCl(CH_2Ph)(H_2)(PCy_3)_2$. ^{1}H NMR (300 MHz, C_6D_6, 20 °C): δ −8.45 (br, 2H), 1.20−2.20 (m, 66H, PCy_3), 4.27 (t, J_{PH} = 3.6 Hz, $PhCH_2$), 7.01 (m, 3H, Ph), 7.72 (d, J_{H-H} = 7.6 Hz, 2H, Ph ortho). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6, 20 °C): δ 18.3 (s). The lifetime of this compound was too short to allow T_1 measurement. After 18 h, an orange solution was obtained and the ^{1}H and ^{31}P{^{1}H} NMR spectra show clean conversion to $RuHCl(N_2)(PCy_3)_2$ and toluene. Spectroscopic data for $RuHCl(N_2)(PCy_3)_2$. ^{1}H NMR (300 MHz, C_6D_6, 20 °C): δ −27.26 (t, J_{P-H} = 18.3 Hz, Ru−H), 1.22−2.59 (m, 66H, PCy_3). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6, 20 °C): δ 43.7 (s; doublet under off-resonance conditions). IR (C_6D_6, cm^{-1}): ν(N≡N) 2060. The extreme air sensitivity of this compound resulted in unsatisfactory elemental analysis determinations.

Reaction of $Ru(H)_2(N_2)_2(PCy_3)_2$ with C_6F_6: Formation of $RuHF(N_2)(PCy_3)_2$. To a freshly prepared solution of $Ru(H)_2(N_2)_2(PCy_3)_2$ (9.4 mg, 0.013 mmol) in C_6D_6 (0.5 mL) placed in an NMR tube was added C_6F_6 (3 μL, 0.026 mmol) via syringe. After 18 h, ^{1}H and ^{31}P NMR spectroscopies showed clean conversion to $RuHF(N_2)(PCy_3)_2$. In the ^{1}H and ^{19}F NMR spectra peaks corresponding to C_6F_5H were observed. ^{1}H NMR (300 MHz, C_6D_6, 20 °C): δ −25.39 (broad triplet, J_{P-H} = 17 Hz, Ru−H), 1.06−2.36 (m, 66H, PCy_3). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6, 20 °C): δ 47.4 (d, J_{P-F} = 20.4; under off-resonance conditions: vt, $J_{P-F} = J_{P-H}$ = 20 Hz). ^{19}F NMR (279 MHz, C_6D_6, 20 °C): δ −306.7 (br, Ru−F). IR (C_6D_6, cm^{-1}): ν(N≡N) 2054 (s), ν(Ru−H) 2039 (w).

Reaction of $Ru(H)_2(N_2)_2(PCy_3)_2$ with BrCH═CHPh: Formation of $RuHBr(N_2)(PCy_3)_2$. To a solution of $Ru(H)_2(N_2)_2(PCy_3)_2$ (11 mg, 0.015 mmol) in C_6D_6 (0.5 mL) placed in an NMR tube, BrCH═CHPh (2 μL, 0.015 mmol) was added via syringe. After 10 min ^{1}H and ^{31}P NMR spectroscopies show clean conversion to $RuHBr(N_2)(PCy_3)_2$. In the ^{1}H NMR spectrum, together with the peaks corresponding to the Ru compound, were observed signals assigned to styrene by comparison with a pure sample. Spectroscopic data of $RuHBr(N_2)(PCy_3)_2$. ^{1}H NMR (C_6D_6, 300 MHz, 20 °C): δ −27.51 (t, J_{P-H} = 18.3 Hz, 1H, Ru−H), 1.04−2.67 (m, 66H, PCy_3). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6, 20 °C): δ 42.6 (s). IR (C_6D_6, cm^{-1}): ν(N≡N) 2060.

Reaction of $Ru(H)_2(N_2)_2(PCy_3)_2$ with CH_3I: Formation of $RuHI(N_2)(PCy_3)_2$. To a solution of *freshly* prepared $Ru(H)_2(N_2)_2(PCy_3)_2$ (18.3 mg, 0.025 mmol) in C_6D_6 (0.5 mL), CH_3I (2 μL, 0.025 mmol) was added via syringe, causing an immediate color change from yellowish to brown, accompanied by gas evolution. The ^{1}H and ^{31}P{^{1}H} NMR spectra recorded after 10 min show quantitative conversion to $RuHI(N_2)(PCy_3)_2$. In addition, the ^{1}H NMR spectrum shows a singlet at 0.13 ppm, assigned to methane. ^{1}H NMR (C_6D_6, 300 MHz, 20 °C): δ −27.65 (t, J_{P-H} = 17.8 Hz, 1H, Ru−H), 0.90−2.80 (m, 66H, PCy_3). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6, 20 °C): δ 41.2 (s). IR (C_6D_6, cm^{-1}); ν(N≡N) 2062.

Reaction of $RuHCl(N_2)(PCy_3)_2$ with H_2. A solution of $RuHCl(N_2)(PCy_3)_2$ in C_6D_6 was placed in an NMR tube fitted with a Teflon closure. The solution was frozen in liquid N_2, the headspace was evacuated, and it was filled with H_2 (1 atm), ^{1}H and ^{31}P{^{1}H} NMR spectra recorded after 20 min showed quantitative conversion to $RuHCl(H_2)(PCy_3)_2$.

Reaction of $RuHCl(N_2)(PCy_3)_2$ with CO. A solution of $RuHCl(N_2)(PCy_3)_2$ in C_6D_6 was placed in an NMR tube fitted with a Teflon closure. The solution was frozen in liquid N_2, the headspace was evacuated, and it was filled with CO (1 atm). Upon warming immediate color change from orange to very pale yellow was observed. ^{1}H and ^{31}P{^{1}H} NMR recorded after 20 min showed the presence of two products: $RuHCl(N_2)(CO)(PCy_3)_2$ and $RuHCl(CO)_2(PCy_3)_2$[12] in a ratio of 1:1. After 8 h, the ratio among this two products was 3:7, and only after 44 h under CO atmosphere, $RuHCl(CO)_2(PCy_3)_2$ was the only compound present in the solution.

Spectroscopic data for $RuHCl(N_2)(CO)(PCy_3)_2$: ^{1}H NMR (300 MHz, C_6D_6, 20 °C): δ −3.97 (t, J_{P-H} = 20.7, 1H, Ru−H), 1.10−2.40 (m, 66H, PCy_3). ^{31}P{^{1}H}NMR (121.4 MHz, C_6D_6, 20 °C): δ 48.7 (s).

Reaction of $RuHF(N_2)(PCy_3)_2$ with H_2. A solution of $RuHF(N_2)(PCy_3)_2$ in C_6D_6 was placed in an NMR tube fitted with a Teflon closure. The solution was frozen in liquid N_2, the headspace was evacuated, and it was filled with H_2. Upon warming, immediate color change from orange to yellowish was observed. ^{1}H and ^{31}P{^{1}H} NMR spectroscopies showed quantitative formation of $Ru(H)_2(H_2)_2(PCy_3)_2$.[8]

Results

The work of Chaudret,[8,11,15] who established that RuH_6L_2 (L = PCy_3) is in fact $Ru^{II}(H)_2(H_2)_2L_2$, revealed that this divalent Ru complex is nevertheless a reducing agent, subject to oxidative addition of C−Cl and C−I bonds (e.g., CH_3I, PhI, or excess CH_2Cl_2) to give RuH_3XL_2, which is *still* a complex of Ru^{II}/$RuHX(H_2)L_2$. A full mass balance of this reaction type is lacking: the fate of the R moiety in R−X and of the hydride and H_2 ligands is not established. The mechanism is also unknown.

CH_2Cl_2 as a Carbene Source. We find that RuH_6L_2 reacts with CH_2Cl_2 slowly (3 h) under argon at 25 °C in pentane to give $RuCl_2(CH_2)L_2$ (63% isolated yield). If the crude suspension was dried under vacuum, its ^{1}H and ^{31}P NMR spectra showed the presence of some $RuHCl(H_2)L_2$ (around 15%) together with the major product $RuCl_2(=CH_2)L_2$.[13] It was shown independently that $RuCl_2(CH_2)L_2$ reacts with H_2 (1 atm) in benzene over a period of 18 h at 25 °C to give $RuHCl(H_2)L_2$,[11,12] CH_4, and HCl. Given the fact that RuH_6L_2 reacts with HCl to give $RuHCl(H_2)(PCy_3)_2$ (see Experimental Section), equimolar $RuH_2(H_2)_2(PCy_3)_2$ was added to the reaction of $RuCl_2(CH_2)L_2$ and H_2 as a trapping reagent of the released HCl. Under these conditions, only $RuHCl(H_2)(PCy_3)_2$ was formed (Scheme 1).

Scheme 1

$$RuCl_2(CH_2)L_2 + 3\,H_2 \longrightarrow RuHCl(H_2)L_2 + CH_4 + HCl$$

$$Ru(H)_2(H_2)_2L_2 + HCl \longrightarrow RuHCl(H_2)L_2 + 2\,H_2$$

$$\text{Overall: } RuCl_2(CH_2)L_2 + Ru(H)_2(H_2)_2L_2 + H_2 \longrightarrow 2\,RuHCl(H_2)L_2 + CH_4$$

Also, the addition of a stoichiometric amount of NEt_3 to the reaction of $RuCl_2(CH_2)L_2$ with H_2 leads to $RuHCl(H_2)L_2$, $[HNEt_3]Cl$, and CH_4.

Thus, H_2 released in the presumed eq 4 undergoes a secondary reaction to consume the primary product. In fact, when the

$$Ru(H)_2(H_2)_2L_2 + CH_2Cl_2 \rightarrow RuCl_2(CH_2)L_2 + 3H_2 \quad (4)$$

reaction of $Ru(H)_2(H_2)_2L_2$ with CH_2Cl_2 (ratio 1:2) is carried out in an NMR tube (*closed system*) after 15 min we observe, in the ^{31}P NMR spectrum, peaks corresponding to $Ru(H)_2(H_2)_2L_2$ (90%), $RuCl_2(=CH_2)(PCy_3)_2$ (5%), and $RuHCl(H_2)(PCy_3)_2$ (5%). Monitoring the reaction by ^{1}H and ^{31}P NMR spectroscopies over a period of 24 h reveals that (under these conditions) $RuCl_2(=CH_2)(PCy_3)_2$ never constitutes more than 20% of the ruthenium-containing compounds. It also reveals how the decrease in the amount of $Ru(H)_2(H_2)_2L_2$ in the mixture is accompanied by an increase in the amount of $RuHCl(H_2)(PCy_3)_2$, which is, after 24 h, the only Ru-containing product present in the solution. This confirmed that, as $RuCl_2(CH_2)L_2$ is formed, it undergoes a reaction with the released H_2 present in the reaction medium, giving rise to $RuHCl(H_2)(PCy_3)_2$. This is presumably why, in the earlier report,[11,12] RuH_6L_2 reacts with halocarbons to give simply $RuHX(H_2)L_2$ and why no carbene product was reported.

The reaction of $RuH_2(H_2)_2L_2$ with CH_2Cl_2 exhibits some curious behavior whose origin furnishes mechanistic insight:

(15) Arliguie, T.; Chaudret, B.; Morris, R. H.; Sella, A. *Inorg. Chem.* **1988**, *27*, 598.

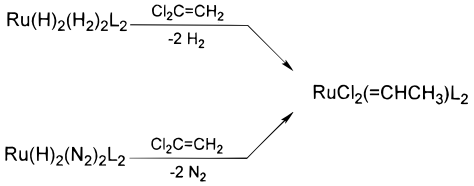
the reaction proceeds to completion (3 h) in a round-bottom flask with a considerable headspace, while in an NMR tube, the reaction is much slower (i.e., after 3 h, there is still $RuH_2(H_2)_2L_2$ (60%) present in the solution). Working on the hypothesis that this represented competitive inhibition by the gaseous product, H_2, the reagents were combined in 5 mL of pentane in a 100 mL reaction flask under 1 atm H_2; there was then no reaction over 3 h at 25 °C. This suggests a mechanism dissociative in H_2, with only the unsaturated product of the preequilibrium (eq 5) being reactive with CH_2Cl_2. This rules

$$Ru(H)_2(H_2)_2L_2 \rightleftharpoons Ru(H)_2(H_2)L_2 + H_2 \qquad (5)$$

out an outer-sphere electron-transfer mechanism and implicates an adduct, $Ru(H)_2(H_2)(\eta^1\text{-}CH_2Cl_2)L_2$, on the path to the first C−Cl oxidative addition. Reaction of $RuH_2(H_2)_2L_2$ with CD_2Cl_2 gave only $RuCl_2(CD_2)L_2$ (by ^1H and ^2H NMR), and so excludes any hydrogen scrambling in the reaction. It was found that all $RuH_2(H_2)_2L_2$ was consumed at a CH_2Cl_2/Ru stoichiometry as low as 1.5:1, but, for reasons of convenient rate, reactions were generally run at 3:1.

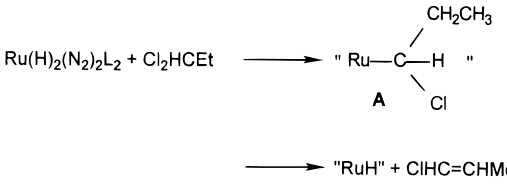
A Ru Source of Decreased H Content. The combination of competitive inhibition and carbene complex consumption by released H_2 led us to seek an alternative ruthenium reagent. $Ru(H)_2(N_2)_2L_2$, formed immediately on exposing a solution of $RuH_2(H_2)_2L_2$ to N_2, is an improvement. It reacts reproducibly and rapidly (20 min) with CH_2Cl_2 at 25 °C in pentane to give cleanly $RuCl_2(CH_2)L_2$. Since the primary reaction is faster, earlier workup is possible; this, together with the lower amount of released H_2 accounts for this improvement.

Other *gem*-Dihalides. We tested the ability of vinylic gem-dichlorides to participate in the reaction. Both $Ru(H)_2(H_2)_2L_2$ and $Ru(H)_2(N_2)_2L_2$ react (time of mixing at room temperature) with $Cl_2C{=}CH_2$ in pentane to give $RuCl_2(=CHCH_3)L_2$ in good yields (eq 6). When the reaction of $Cl_2C{=}CH_2$ with $Ru(H)_2(N_2)_2(PCy_3)_2$ is carried out in an NMR tube, the reaction is quantitative and occurs in time of mixing. By mixing the reagents in an NMR tube at low temperature (−78 °C) and then putting it into an NMR precooled probe, no intermediate could be observed. There is no trace of a vinylidene intermediate: $RuCl_2(=C{=}CH_2)(PCy_3)_2$. The H_2 released in the reaction thus participates in a secondary reaction, and one which is highly selective for C=C over Ru=C unsaturation. When the reaction of $Ru(H)_2(H_2)_2L_2$ with $Cl_2C{=}CH_2$ is carried out in an NMR tube (*closed system*) instead of a Schlenk flask, a secondary reaction takes place more slowly between the released H_2 and $RuCl_2(=CHCH_3)L_2$ to give $Ru(H)_2Cl_2L_2$[16] and ethane.



Other aliphatic *gem*-dichloride compounds were examined to establish the scope of this reaction. Benzylidene chloride, $PhHCCl_2$, reacts with $Ru(H)_2(N_2)_2L_2$ in benzene-d_6 at 25 °C to give $RuCl_2(CHPh)L_2$ (65%), $Ru(H)_2Cl_2L_2$ (7%) and $RuHCl(H_2)L_2$ (28%).

Reaction of $Ru(H)_2(N_2)_2L_2$ with 1,1-dichloropropane in benzene-d_6 at 25 °C gives a mixture of products whose composition varies with time. $RuCl_2(=CHCH_2CH_3)L_2$ was detected as a minor product at short reaction times, together with unreacted starting material. After 24 h, there is no trace of $RuCl_2(=CHCH_2CH_3)L_2$ and in the $^{31}P\{^1H\}$ NMR spectrum, there is a new peak at 43.7 ppm. In the high-field region of the ^1H NMR spectrum, we observe a new triplet at −27.26 ppm. This chemical shift suggests that it is trans to a vacant site. In the IR spectrum, there is a strong band at 2060 cm^{-1} that is within the range of $\nu(N{\equiv}N)$ stretching frequencies. We assign all these spectroscopic data as belonging to the complex $RuHCl(N_2)(PCy_3)_2$. This reaction is understood (eq 7) in terms of the



(7)

primary product **A** having β-hydrogens that can migrate to Ru at a rate competitive with the second C−Cl scission. This new behavior arises because this is the first *gem*-dihalide employed here that offers the possibility of such β-hydrogen migration.

Reactivity of a Monochloride. To support the supposition that *gem*-dichloro compounds react via a two-step mechanism, we investigated the reaction of a monochloro reagent, benzyl chloride. $Ru(H)_2(N_2)_2L_2$ reacts with $PhCH_2Cl$ to give a product that shows a ^1H NMR triplet at 4.27 ppm (J_{P-H} = 3.6 Hz) and a doublet at 7.72, corresponding, respectively, to the benzyl and ortho phenyl protons of a benzyl ligand, assigned to $RuCl(CH_2Ph)(H_2)(PCy_3)_2$. After 18 h, the reaction solution has transformed completely, yielding an orange solution, and shows toluene and $RuHCl(N_2)(PCy_3)_2$.

Preparation of $RuHX(N_2)(PCy_3)_2$ (X = F, Cl, Br, I). We next explored routes to the full set of halo complexes $RuHX(N_2)L_2$. The compound $Ru(H)_2(N_2)_2(PCy_3)_2$ reacts with C_6F_6, $PhCH_2Cl$, $BrCH{=}CHPh$ and CH_3I (under N_2 atmosphere) to give $RuHX(N_2)(PCy_3)_2$ and C_6F_5H (X = F), $PhCH_3$ (X = Cl), $PhCH{=}CH_2$ (X = Br), or CH_4 (X = I) in quantitative yields. The complexes $RuHX(N_2)(PCy_3)_2$ are extremely air sensitive in solution and in the solid state. In the ^1H NMR spectra, the most characteristic feature is a triplet at very high field, with a phosphorus coupling constant of about 18 Hz. The IR spectra exhibit a strong $\nu(N{\equiv}N)$ stretching band. This band, like the $\nu(CO)$ band in the complexes $RuHX(CO)(P^tBu_2Me)_2$, is a gauge of the donor ability of the X ligand. According to the values found, we can estimate that $\sigma{+}\pi$ donation increases in the order: I < Br ∼ Cl < F, which agrees with previous estimations based on $\nu(CO)$.[17] The coordinated nitrogen ligand in $RuHCl(N_2)(PCy_3)_2$ is readily replaced by H_2, giving the known complex $RuHCl(H_2)(PCy_3)_2$. However, when the same reaction is carried out with $RuHF(N_2)(PCy_3)_2$, $Ru(H)_2(H_2)_2(PCy_3)_2$ is obtained; the Ru−F bond is thus subject to hydrogenolysis, forming HF, under very mild conditions.

These results contrast to those for *gem*-dihalide and serve to show that the species $RuX(CR_2Y)(H_2)L_2$ react more rapidly by C−Y oxidative addition to Ru when Y = Cl, while hydrogenolysis (by coordinated H_2) of the Ru−C bond is the primary reaction when Y = H.

Discussion

In a recent synthetic report with the same goal as ours, it was concluded that the zerovalent reagent tested for reaction

(16) A P^iPr_3 analogue has been reported: Grünwald, C.; Gevert, O.; Wolf, J.; González-Herrero, P.; Werner, H. *Organometallics* **1996**, *15*, 1960.

(17) Poulton, J. T.; Sigalas, M. P.; Folting, K.; Streib, W. E.; Eisenstein, O.; Caulton, K. G. *Inorg. Chem.* **1994**, *33*, 1476.

with *gem*-dihalides, Ru(COD)(COT) (COD = 1,5-cyclooctadiene; COT = cyclooctatriene), suffered several limitations, and RuH(olefin)(η^2-P∼C)(PCy_3), a molecule where a PCy_3 C−H bond has oxidatively added to the metal, yielding Ru(II), showed superior performance. Confronted with the same need to "create" reducing equivalents at the metal, C−H reductive elimination, stimulated by the $RHCX_2$ reagent, became the source of Ru(0). However, the olefin incorporated in this synthesis can then undergo olefin metathesis with the first-formed ruthenium carbene, to "lose" the primary product Ru=CHR. Thus, both that report (olefin) and ours (H_2) must deal with the fact that "leaving groups" on the ruthenium source are not benign.

The strategy for generation of carbene complexes from *gem*-dichlorides is attractive, yet it has not been widely exploited. Why is synthesis of $Cp_2W(CPh_2)$ not already reported from $Cp_2W(CO)$ and Cp_2TiCH_2 from $Cp_2Ti(CO)_2$ or $Cp_2Ti(C_2H_4)$? Our success clearly relies in part on the fact that $RuCl_2(CRR')L_2$ contains, as ligands, the entirety of a $RR'CCl_2$ reagent; no chloride need be lost, and the carbene complex has a relatively high formal oxidation number. However, the reagents employed illustrate several *general* features which should be recognized in any attempt to generalize the synthesis of carbene complexes from *gem*-dihalides. The need for coordination of $RR'CCl_2$[18] prior to C−Cl cleavage helps to avoid outer-sphere electron transfer, with the associated uncontrolled character of the resulting radicals. The empty metal orbital allows coordination of both C and Cl after C−Cl bond scission, which would not be true for a saturated metal complex (e.g., $Cp_2W(CO)$). Thus, both N_2 and intact (i.e., preformed) H_2 in $Ru(H)_2(N_2)_2L_2$ and $Ru(H)_2(H_2)_2L_2$ represent "good leaving groups". Perhaps ethylene and other olefins and even arenes (i.e., $(C_6H_6)RuL_2$) could serve this role in future efforts. However, H_2 is also a liability in being reactive toward the resulting unsaturated ruthenium carbene. At least 1 mol of H_2 is absolutely fundamental to the success of this synthetic route, however. It keeps the ruthenium *initially* at the poorly reducing divalent state, to avoid outer-sphere electron transfer. However, during or after the first C−Cl oxidative addition, the $Ru^n(H)_2$ can undergo intramolecular redox change to $Ru^{n-2}(H_2)$, thereby supplying the reducing equivalents (and leaving group) needed for the second C−Cl scission.

With this background, some candidates for four-electron oxidative addition of *gem*-dihalides are $Pt(C_2H_4)_3$, $L_2Pt(H)_2$, $L_2Ru(\eta^3$-styrene$)_2$ and all polyhydride complexes MH_mL_n. Particularly since non-heteroatom-stabilized carbene complexes of the late transition metals are not abundant, this could be a rewarding effort.

In the early days of olefin metathesis catalysis, one catalyst recipe involved $W(CO)_6$ with CCl_4. While it was never verified that $W(CCl_2)(CO)_5$ or $W(CCl_2)Cl_2(CO)_4$ was actually formed, the fact that the $Ru(CRR')Cl_2L_2$ species synthesized here *are* olefin metathesis catalysts[19] suggests that a broader study of this synthetic route with middle and late transition metals could impact this hydrocarbon transformation.

Acknowledgment. This work was supported by the U.S. National Science Foundation. M.O. thanks the Spanish Ministerio de Educación y Cultura for a postdoctoral fellowship. We also thank Johnson Matthey/Aesar for material support.

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(18) CH_2Cl_2 has been shown to be a monodentate and even a bidentate ligand to Ag^+, to Ru^{2+}, and to Ru^0. See: (a)Huang, D.; Huffman, J. C.; Bollinger, J. C.; Eisenstein, O.; Caulton, K. G., *J. Am. Chem. Soc.* **1997**, *119*, 7398. (b) Kulawiec, R. J.; Crabtree, R. H. *Coord. Chem. Rev.* **1990**, *99*, 89.

(19) (a) Grubbs, R. H. *Pure Appl. Chem.* **1994**, *A31*, 1829. (b) Dias, E. L.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1997**, *119*, 3887 and references therein. (c) Grubbs, R. H.; Miller, S. J.; Fu, G. C. *Acc. Chem. Res.* **1995**, *28*, 446.