Reaction between Ethylene and Cycloruthenated Tertiary Amines: Stoichiometric Olefin Arylation and Stereospecific One-Carbon-Atom Insertion

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Ethene has been reacted under mild conditions with the benzene cycloruthenated dimethyl(phenylmethyl)amine compounds [Ru(η^6-C_6H_6){2-(CH_2NMe_2-κN)-C_6H_4-κC^1}L]$^+$ (**1a**, L = Cl^-; **1b**, L = NCMe), obtained via intramolecular C−H activation. The stoichiometric arylated olefin dimethyl((2-ethenylphenyl)methyl)amine (**2**) and/or new organometallic species resulting from the overall insertion of one carbon atom into the Ru−C bond, [Ru(η^6-C_6H_6){1-(CHMe-κC)-2-(CH_2NMe_2-κN)-C_6H_4}L]$^+$ (**3a,** L = Cl^-; **3b**, L = NCMe), have been obtained in varying proportions according to the reaction conditions and to the nature of the starting complex. The six-membered metallacycles were found as a single pair of enantiomers of $R_{Ru}R_C$ and $S_{Ru}S_C$ configurations, as established by ^{1}H NOE experiments. In solution under an argon atmosphere, **3a** rearranged to the more stable five-membered ruthenacycle [Ru(η^6-C_6H_6){2-(CH_2NMe_2-κN)-3-Et-C_6H_3-κC^1}Cl] (**4a**). Under ethene pressure, the intramolecular rearrangement is followed by a second ethene insertion into the Ru−C bond, leading to the formation of [Ru(η^6-C_6H_6){1-(CHMe-κC)-2-(CH_2NMe_2-κN)-3-Et-C_6H_3}Cl] (**5a**), the overall reaction being the result of a double C−H activation. A molecule of propene has also been inserted into the Ru−C bond of **1a**. Diastereo- and regiospecific double insertion leading to the formation of [Ru(η^6-C_6H_6){1-(CHEt-κC)-2-(CH_2NMe_2-κN)-3-*i*Pr-C_6H_3}Cl] (**7a**) has been observed. Ethene insertion performed on the benzene ruthenacycle **1a** in deuterated methanol led to stereospecific deuterium incorporation in the six-membered metallacycle **3a** at both carbon atoms of the CHMe unit. These data militate in favor of the reversibility of most elementary steps of the insertion process.

Introduction

The coupling reaction between an aryl unit and an olefin catalyzed by transition metals is one of the most important processes in modern chemistry. The first results describing this C−C bond formation dated back to 1967, when Moritani and Fujiwara reported the synthesis of stilbene, starting with styrene and benzene in the presence of stoichiometric amounts of palladium chloride.[1] This reaction, later extended to aryl halides and alkenes, is now widely known as the Heck reaction.[2] From a green chemistry point of view, the major disadvantage of this process lies in saltlike byproduct formation. These salts originate in the fact that the metal−carbon bond is usually the result of the oxidative addition of R−X on Pd(0) derivatives (X = halides, anionic leaving groups). Consequently, given the importance of this reaction both in organic synthesis and as an industrial procedure, the development of an alternative reaction which would allow the production of direct coupling products between arenes and alkenes via a C−H activation reaction represents one of the major challenges of modern chemistry.[3] Palladium-catalyzed arylation of activated olefins consuming sacrificial oxidants[4,5] or even rhodium-[6] and ruthenium-catalyzed[7] reactions carried out under an oxygen atmosphere have been performed. Even though some of these and related[8] reactions display interesting efficiencies, their industrial applications as novel processes are not yet around the corner, as they require unfriendly reaction conditions such as trifluoroacetic acid as a solvent. Moreover, one of the major disadvantages of these systems is the low regioselectivity observed with substituted aromatic derivatives. A possible answer to this problem is to use chelation-assisted systems, as exemplified by the ruthenium-[9] and pal-

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ladium-catalyzed[10] ortho-vinylation of aromatic imines, imidates, and amides. It was believed that the unsaturated coupling compounds were formed by β-H elimination from a carbometalation intermediate resulting from olefin insertion into a metal−carbon bond. This hypothesis was confirmed by a stoichiometric reaction between a cycloruthenated dimethyl(phenylmethyl)amine complex and ethene that was first reported in a preliminary form.[11] Further results concerning the insertion reaction are now described here. Reaction conditions have been screened: various solvents, including CD_3OD, and different substrates have been used. Rearrangement and double-insertion processes have been examined. Mechanistic proposals are made to rationalize the experimental facts.

Results

Preliminary Observations. We reported previously[11] that the reaction between ethene and the cycloruthenated compound [Ru(η^6-C_6H_6){2-(CH_2NMe_2-κN)-C_6H_4-κC^1}L] (**1a,** L = Cl^-; **1b**, L = CH_3CN) in methanol afforded dimethyl((2-ethenylphenyl)methyl)amine (**2**), together with the six-membered cycloruthenated complex [Ru(η^6-C_6H_6){1-(CHMe-κC)-2-(CH_2NMe_2-κN)-C_6H_4}L], **3a** (L = Cl^-) or **3b** (L = CH_3CN) with a total conversion. The organic product **2** was the C−C coupling product from a Heck reaction performed through C−H activation, and the organometallic compounds **3a** and **3b** resulted from the overall insertion of one carbon atom into the Ru−C bond of the starting material. The yields of **2** and **3a** were respectively 81 and 19% and those of **2** and **3b** respectively 15 and 85%. However, after publication of these preliminary results we observed that, in the particular case of **1a**, they were only reproducible using one given batch of MeOH. Using many different batches of this solvent led, with a high reproducibility, to a reverse chemoselectivity: i.e., similar to that observed with **1b** (see Table 1, entries 1 and 2; the chemoselectivity factor (α) reported in Table 1 is the ratio of the organic material **2** versus the organometallic compounds **3a** and **3b**). All batches of MeOH were distilled over $Mg(OMe)_2$, and our efforts trying to rationalize this behavior, i.e. by modifying the pH, were in vain. We thus decided to carefully reinvestigate this reaction by studying the influence of many parameters upon the course of the reaction with an emphasis, inter alia, upon the role of the solvent. Note that no reaction was ever observed with the compound [Ru(η^6-C_6H_6)-{2-(CH_2NMe_2-κN)-C_6H_4-κC^1}PMe_2Ph]$^+$-PF_6^- (**1c**) (Table 1, entry 3).

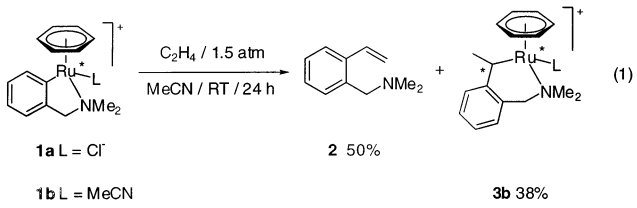
Reaction in EtOH. The reaction between either **1a** or **1b** and ethene in different batches of ethanol, all distilled over magnesium prior to use, led to mixtures of **2** and **3a** or **3b** with yields similar (Table 1, entries 4 and 5) to those obtained with the novel batches of MeOH.

Reaction in CH_3CN. Acetonitrile proved to be the best choice of solvent, as it led to clear-cut results as far as selectivity is concerned. When a suspension of the cycloruthenated complex **1a** was stirred for 24 h in MeCN at room temperature in the presence of ethene (1.5 atm), dimethyl((2-ethenylphenyl)methyl)amine (**2**) was formed selectively with a 50% conversion. With **1b** as the starting material, only the six-membered cycloruthenated complex **3b** was obtained with a 38% conversion after 20 h of reaction (eq 1; Table 1, entries 6 and 7). The complex **3b** was fully characterized by ^1H and ^{13}C NMR and elemental analysis.

Table 1. Chemoselectivity of the Insertion Reaction[a]

entry no.	starting complex	solvent	additive	conversn in **2** (%)	conversn in **3** (%)	selectivity factor α
1	**1a**	MeOH		20[b]	80[c]	0.25
2	**1b**	MeOH		15	85	0.18
3	**1c**	MeOH		0	0	
4	**1a**	EtOH		10	90	0.11
5	**1b**	EtOH		20	80	0.25
6	**1a**	MeCN		50	0	>50
7	**1b**	MeCN		0	38	<0.05
8	**1a**	MeCN	dmba (1 equiv)	50	0	>50

[a] All the reactions were run under 1.5 atm of ethene for 1.5 h, except for entries 6 (24 h), 7 (20 h), and 8 (48 h). [b] Averaged values obtained by performing the reaction with 5 different batches of MeOH (conversions observed were in the range 5−35%). [c] Averaged values obtained by performing the reaction with 5 different batches of MeOH (conversions observed were in the range 95−65%).



(1)

It is important to note that despite the fact that **3a** and **3b** are not indefinitely stable in solution (see later) they never led to a β-elimination process to afford **2**.

In half-sandwich ruthenium compounds akin to those studied here, the ruthenium atom is a center of chirality. After ethene insertion into the Ru−C bond of **1a** and **1b**, the ruthenated carbon atoms of **3a** and **3b** are also asymmetric centers. Interestingly, ^1H NMR spectra of both six-membered metallacyclic compounds **3a** and **3b** disclosed one racemic mixture only. As we could not get crystals of either **3a** or **3b** suitable for X-ray diffraction studies, the structure of **3a** was established by ^1H NOE experiments in solution. This study allowed us to suggest a boat conformation for the six-membered metallacyclic unit: the methyl substituent of the asymmetric carbon was found at an equatorial position, interacting with the aromatic ligand on one side and with the benzene ring on the other side. The benzene ring itself occupies a pseudoaxial position and interacts with one of the *N*-methyl groups (Figure 1). It was thus concluded that the two enantiomers displayed $R_{Ru}R_C$ and $S_{Ru}S_C$ configurations[12] (see the Supporting Information).

Compound **3a** is unstable and isomerizes slowly under argon in MeOH solution to yield the new cycloruthen-

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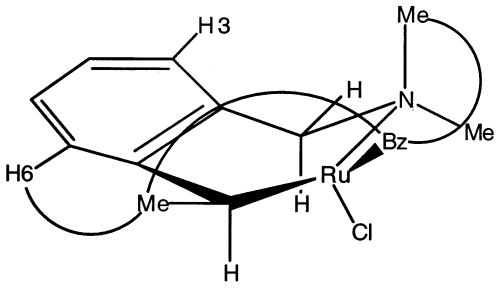
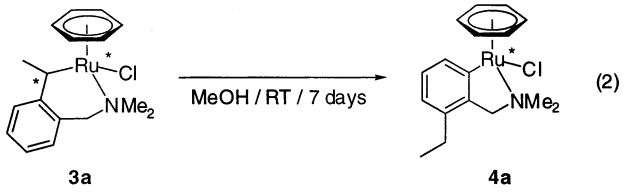


$(S)_{Ru}(S)_C$ -**3a**

Figure 1. Conformation and configuration of **3a** established by ^{1}H NOE analysis.

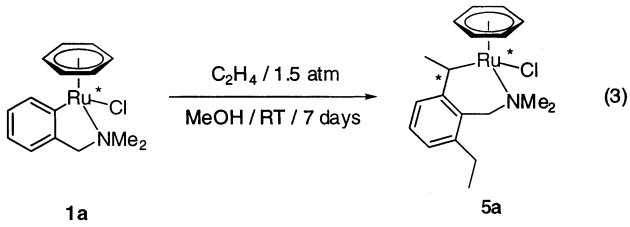
ated complex [Ru(η^6-C_6H_6){2-(CH_2NMe_2-κN)-3-Et-C_6H_3-κC^1}]Cl (**4a**) (eq 2). The presence of an *o*-ethyl substit-



(2)

uent and the occurrence of a five-membered metallacyclic unit in **4a** were unambiguously established from ^{1}H and ^{13}C NMR data.

This new organoruthenated species arose from the cleavage of the Ru−C bond in **3a** and the activation of a second C−H aromatic bond. It followed that the insertion of a second ethene molecule should be possible. Indeed, when **4a** was treated under ethene pressure, the orange compound [Ru(η^6-C_6H_6){1-(CHMe-κC)-2-(CH_2NMe_2-κN)-3-Et-C_6H_3}Cl] (**5a**) was isolated in 24% yield after 7 days (eq 3). This compound has been



(3)

characterized by ^{1}H and ^{13}C NMR spectrometry and elemental analysis. The ^{1}H and ^{13}C NMR assignments were confirmed by 2D COSY and ^{1}H/^{13}C HSQC measurements. 2D ROESY analysis established the same boat conformation and stereochemistry as those found for **3a** (see the Supporting Information).

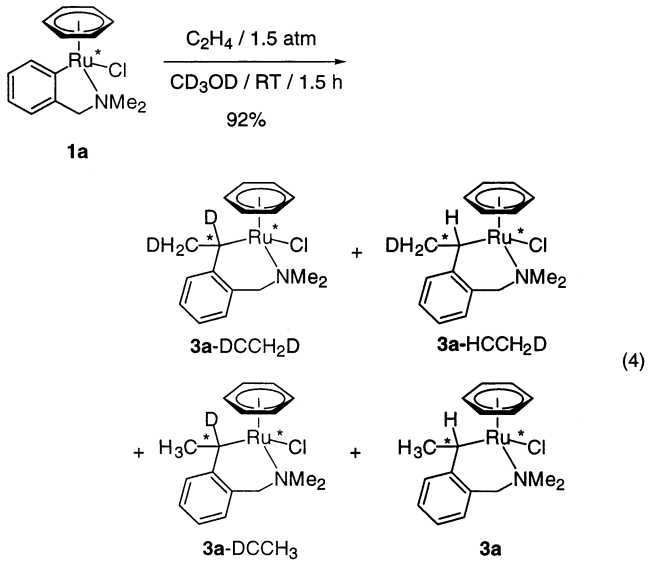
Reaction in the Presence of 1 Equiv of Ligand. To test whether a catalytic olefin arylation would be possible, 1 equiv of dimethyl(phenylmethyl)amine (dmba) was added to the reaction in acetonitrile. No modification was observed, except a decreased rate of the reaction (50% of product **2** after 48 h; Table 1, entry 8).

Deuterium Labeling. Performing the reaction of the complex **1a** with ethene in CD_3OD afforded organometallic deuterated derivatives. Analyzing both the ^{2}H NMR spectrum in $CHCl_3$ and the ^{1}H NMR spectrum in $CDCl_3$ (Figure 2) led us to the following conclusions.

(a) The same amount of deuterium has been equally incorporated at the CH and the methyl groups of the ruthenated CHMe unit; i.e., half of the protons and one-sixth of the methyl protons have been substituted by deuterium atoms.

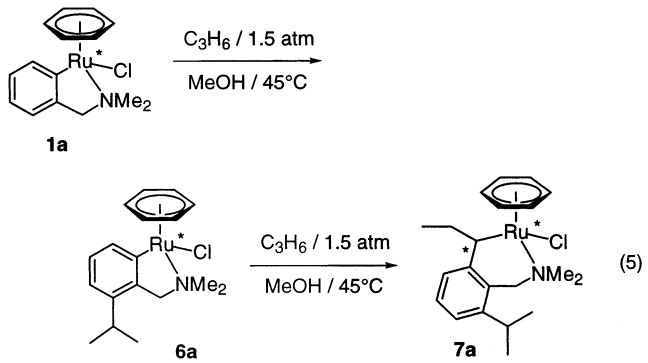
(b) The chemical shifts of the new deuterated species indicate that the same $R_{Ru}R_C$ and $S_{Ru}S_C$ enantiomeric pair as for the nondeuterated species (see above) was obtained.

(c) The analysis of the signal shape of the ^{1}H NMR spectrum (see the Supporting Information) of the two groups of protons pointed to the presence of a 1:1:1:1 mixture of **3a**, **3a**-$DCCH_3$, **3a**-$HCCH_2D$, and **3a**-$DCCH_2D$ (eq 4).



(4)

Propene Insertion. Among the other olefins used, only propene was reactive. The reaction was performed at 45 °C. After 3 h a fairly good yield of the compound [Ru(η^6-C_6H_6){2-(CH_2NMe_2-κN)-3-*i*Pr-C_6H_3-κC^1}]Cl (**6a**) was obtained (40%) (eq 5). Its formation ($t_{1/2}$ = 2.5 h, k_f



(5)

= 0.3 h^{-1}) and subsequent transformation ($t_{1/2}$ = 15.5 h, k_r = 0.04 h^{-1}) in the six-membered complex [Ru(η^6-C_6H_6){1-(CHEt-κC)-2-(CH_2NMe_2-κN)-3-*i*Pr-C_6H_3}Cl] (**7a**)- has been followed versus time (Figure 3). The structure of the nonisolated compound **6a**, as established by ^{1}H and ^{13}C NMR, was found to be closely related to that of an inserted/rearranged organometallic product such as **4a**. Compound **7a** was not isolated in pure form

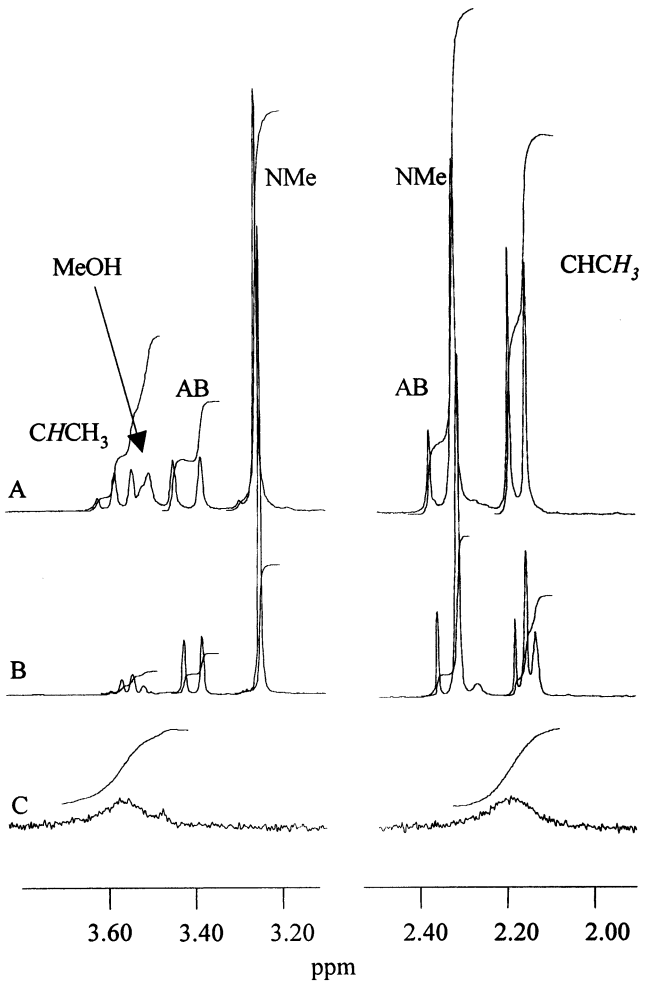


Figure 2. (A) ^{1}H NMR in $CDCl_3$ of **3a** obtained in CH_3OH. (B) ^{1}H NMR in $CDCl_3$ of **3a** obtained in CD_3OD (eq 4). (C) ^{2}H NMR in $CHCl_3$ of **3a** obtained in CD_3OD (eq 4).

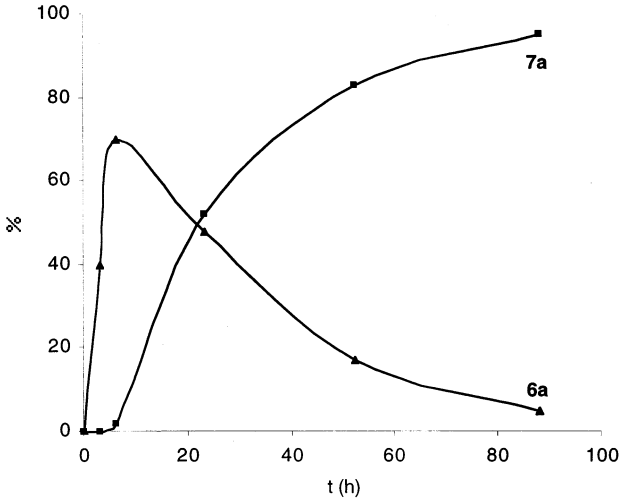
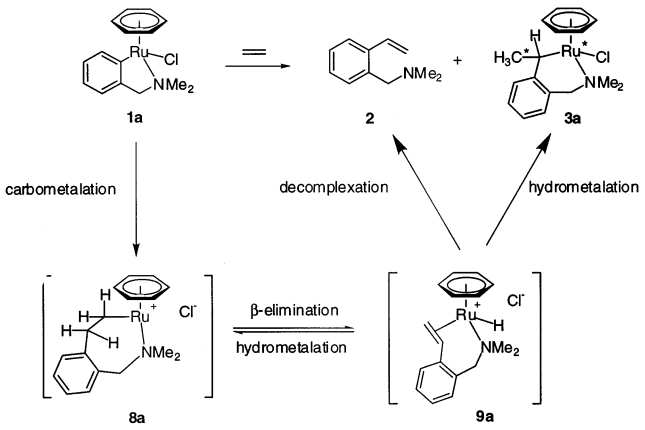


Figure 3. Kinetics of the formation of the intermediate **6a** and of the doubly alkylated compound **7a** (eq 5).

but has been unambiguously characterized by ^{1}H and ^{13}C NMR, the signal assignments being made with the aid of 2D COSY, ^{1}H/^{13}C HSQC, and ^{1}H/^{13}C HMBC. Interestingly, as in the cases of **3a**,**b** and **5a**, only one enantiomeric pair was observed. Its stereochemistry has therefore been investigated by a 2D ROESY experiment, and it has been established that **7a** displays a boat conformation analogous to the other complexes (see the Supporting Information).

Scheme 1. Mechanism of the Reaction between Cycloruthenated dmba and Ethene



The regioselectivity of the two independent insertion reactions of propene in the Ru−C bonds of **1a** and **6a** was quite amazing. Indeed (see the discussion below), whereas **6a** was the result of a 1,2-insertion of propene, **7a** resulted from the opposite regioselectivity (eq 5).

Discussion

Chemoselectivity. PMe_2Ph is a strong ligand that may not be removed from the ruthenium center, whereas chloride and acetonitrile are labile.[13] The consequence for the compounds having the latter ligands is that a vacant coordination site on the Ru atom may be available for ethene. On this basis, a simple mechanism can be drawn (Scheme 1). Ethene is rapidly carbometalated (or inserted into the Ru−C bond of **1a**), and the seven-membered metallacycle **8a**, akin to those observed in related reactions where alkynes were inserted into Ru−C bonds, is formed.[14] A β-elimination process led then to the ethenyl hydridoruthenium intermediate **9a**. Faller and Chase recently isolated and fully characterized a related compound, which contained a styrene ligand bound to a (η^6-cymene)(PR_3)Ru−H unit.[15] This complex arose through an insertion−β-elimination process of ethene into a Ru−Ph moiety. Whereas Faller's compound was rather stable, in our case the existence of **9a** could only be deduced from the nature of its evolution to **2** and **3a**. Thus, the intramolecular coordination of the CH_2NMe_2 group in **9a** is very likely to be responsible for the different behavior of our system as compared to that of Faller.

In MeCN, the chloride ion, which is present in **9a**, is a strong ligand for Ru, because it is not solvated in this solvent. It may thus easily substitute the ethenyl moiety and hence favor the formation of **2**. The benzene chlorohydridoruthenium compound thus obtained was most likely decomposed, as it could never be identified

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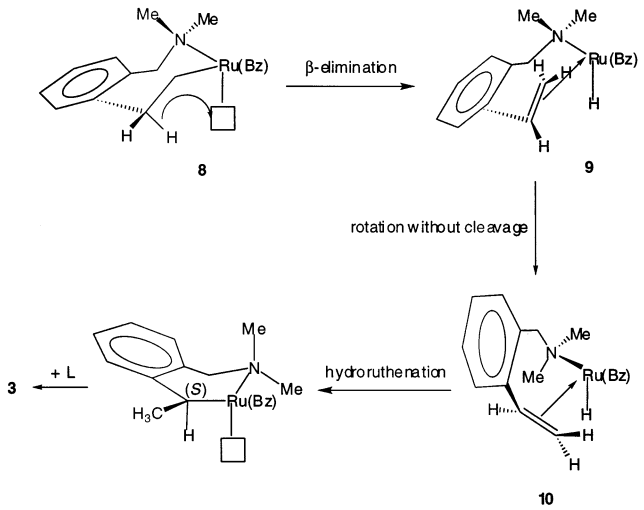
Scheme 2. Reaction Pathway for the Stereospecific One-Carbon-Atom Insertion[a]



[a] The η^6-benzene ligand and the positive charge on Ru are not represented for the sake of clarity.

from the reaction mixture. In the same solvent, for **9b** (L = CH_3CN), due to the absence of chloride, the ethenyl moiety is no longer displaced away from the Ru−H group. Thus, because of the fairly strong intramolecular N−Ru bond, the only evolution of **9b** is the formation of **3b** via a hydroruthenation reaction of the C=C bond. We believe that these facts may rationalize the very high chemoselectivity of the evolution of **9** in MeCN ($\alpha > 50$ with **9a** (L = Cl^-) and $\alpha < 0.05$ with **9b** (L = CH_3CN)). On the other hand, alcohols are protic solvents that solvate the chloride ion via ionic hydrogen bonds, a situation that will obviously decrease its nucleophilicity. Thus, the exchange of the ethenyl ligand with Cl^- should occur less readily and hence the chemoselectivity of the reaction in ROH is much lower than in MeCN.

The presence of the NMe_2 group on the metalated aryl moiety thus has a dramatic influence on the course of the coupling reaction between aryl and ethene. For the first time the occurrence of a stable one-carbon-inserted organometallic product has been observed in these reactions. This feature might be due to the formation, throughout the process, of pseudo-metallacyclic species whose conformations are imposed by the presence of the Me_2N−Ru unit. This could be explained by a Thorpe−Ingold type effect, which is well-known in organic synthesis to favor the formation of carbocyclic units by the presence of *gem*-dimethyl groups.

Stereoselectivity of the One-Carbon-Atom Insertion. We have shown that, in the six-membered metallacyclic ring, the absolute configuration of the novel asymmetric carbon is the same as that of the ruthenium center. Let us suppose that after the insertion of the ethene into the Ru−C bond of **1a** or **1b** the configuration of Ru is *S*. The β-elimination−hydroruthenation of the olefin unit may be rationalized as depicted in Scheme 2. One very likely conformation of the hypothetical seven-membered metalated ring **8**, formed after ethene insertion, could be that of a chair in which the benzyl β-CH_2 group should be close to the vacant coordination site on Ru. This allows one of the protons of this CH_2 to have an agostic interaction with Ru, a situation likely to precede the β-elimination leading to the intermediate **9**. The configuration of the C=C bond thus formed from the Ru atom point of view is *Re*. The step forward to achieve the final product can only occur if the double bond rotates in such way so as to align the $CH=CH_2$ with the Ru−H bond, a process that is akin to a metathesis. Moreover, in order to explain the high stereoselectivity of the reaction, this movement must take place while the Ru atom remains on the *Re* face of the alkene, leading to intermediate **10**. We propose that the movement inside the molecule can occur by changing the chair conformation of the six-membered ring in **9** to a boat-type conformation in **10**, as depicted in Scheme 2. By doing so, the Ru−H vector, which was parallel to the CH_2=CH bond in **9**, becomes antiparallel to this bond in **10**. The hydrometalation of the C=C bond can then take place, leading to the final product **3**, for which the configuration of the novel asymmetric carbon atom is indeed *S*.

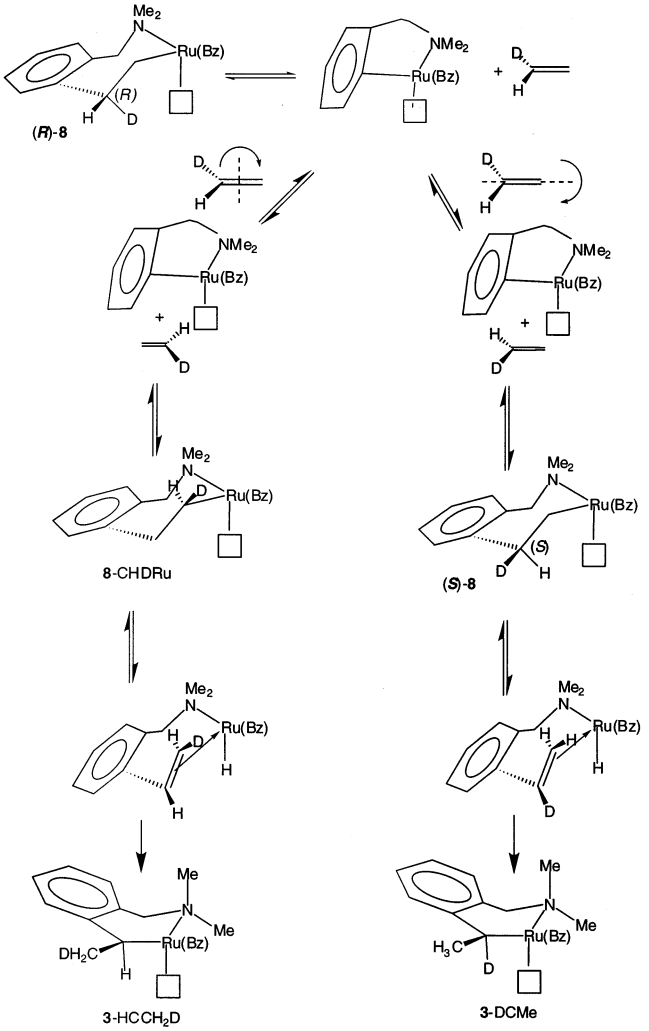
Deuterium Labeling Experiment. The incorporation of deuterium did obviously occur via H−D exchange[16] on the intermediate **9** depicted above. Following the same mechanism (Scheme 2), this explains the partial deuteration of the methyl group in **3a**. However, this can by no means explain the 50% deuteration at the CH unit. Indeed, the reverse reaction of the β-elimination will lead to the intermediate **8**. According to the previous results the configuration of the carbon stereocenter cannot be changed without changing in the same time the configuration of the Ru atom. Therefore, a likely way to perform the deuteration at the benzylic carbon atom is to envisage a reversible extrusion reaction (Scheme 3) that would produce deuterated ethene. Insertion of the latter into the Ru−C bond will lead to the monodeuterated products. Deuterium incorporation has occurred stereospecifically and equally at the CH and the CH_3 units. This fact strongly militates in favor of the latter mechanism. The first mechanism that led to D incorporation at the CH_3 might well be of marginal importance, but it is the only one that accounts for the occurrence of the dideuterated complex **3a**-$DCCH_2D$.

Molecular Rearrangement. The organometallic complex **3a** isomerized slowly to the ethyl-substituted complex **4a**. The demetalation of the six-membered complex and its remetalation to yield a more stable five-membered metallacycle are obviously needed. Such rearrangement has been observed in refluxing benzene with an arene pincer ruthenium complex.[17] It required C−H activation processes based on the NMe_2 decoordination. This may effectively be achieved at high temperature. In our case, as we have shown that the formation of **3a** is stereospecific, the decoordination of the N atom should not be encountered. We thus rather propose, as the determining step of the reaction, a heterolytic cleavage of the Ru−C bond leading to a stabilized benzylic carbanion. This species could be protonated by MeOH to yield an *o*-ethyl dmba derivative that should be ortho metalated by the electrophilic Ru^+ moiety to afford **4a** (see Scheme 4).

(16) Rahmouni, N.; Osborn, J. A.; De Cian, A.; Fischer, J.; Ezzamarty, A. *Organometallics* **1998**,*17*, 2470.

(17) Steenwinkel, P.; James, S. L.; Gossage, R. A.; Grove, D. M.; Kooijman, H.; Smeets, W. J.; Spek, A. L.; van Koten, G. *Organometallics* **1998**, *17*, 4680.

Scheme 3. Reaction Pathway for the Stereospecific Deuteration of the Benzylic Carbon[a]



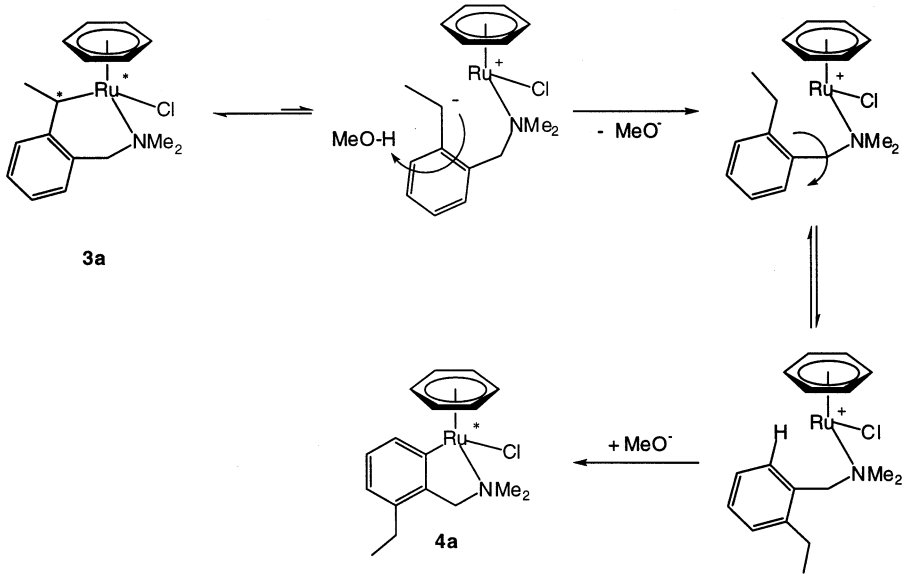
[a] The η^6-benzene ligand and the positive charge on Ru are not represented for the sake of clarity.

Regiospecific Double Insertion. Insertion of a second substrate can be considered as a semicatalytic reaction, as two aromatic C−H bonds have been activated. The propene double-insertion reaction is worth discussing because of its unexpected regioselectivity. The formation of the isopropyl-substituted metallacycle **6a** can only be explained by an initial 1,2-insertion of propene followed by a rapid rearrangement of the intermediate six-membered metallacycle **A** in a more stable five-membered complex (Scheme 5). The direction of this first insertion is uncommon; in general, 2,1-insertions are observed,[5,7] even in chelation-assisted reactions.[9] Examination of molecular models led to the conclusion that 2,1-insertion might be disfavored because of steric interactions between the methyl substituent of the incoming substrate and the benzene ruthenium ligand. Nevertheless, the second insertion is of a 2,1-type. After formation of **6a**, the 1,2-insertion, kinetically favored, should lead to the unstable six-membered metallacycle **B**, which cannot rearrange. As a consequence the only step forward for the system is the way back to the starting ruthenacycle **6a**. Slow 2,1-insertion as the other possible alternative leads to compound **7a**, which is more stable than **B** because the steric interactions between the *n*-propyl and the η^6-benzene groups are minimized. Note that this is in agreement with the observed kinetics of **6a** and **7a** formation. We can thus propose the reaction mechanism depicted in Scheme 5 where all the elementary steps, except the rearrangement of **A** to **6a**, are reversible.

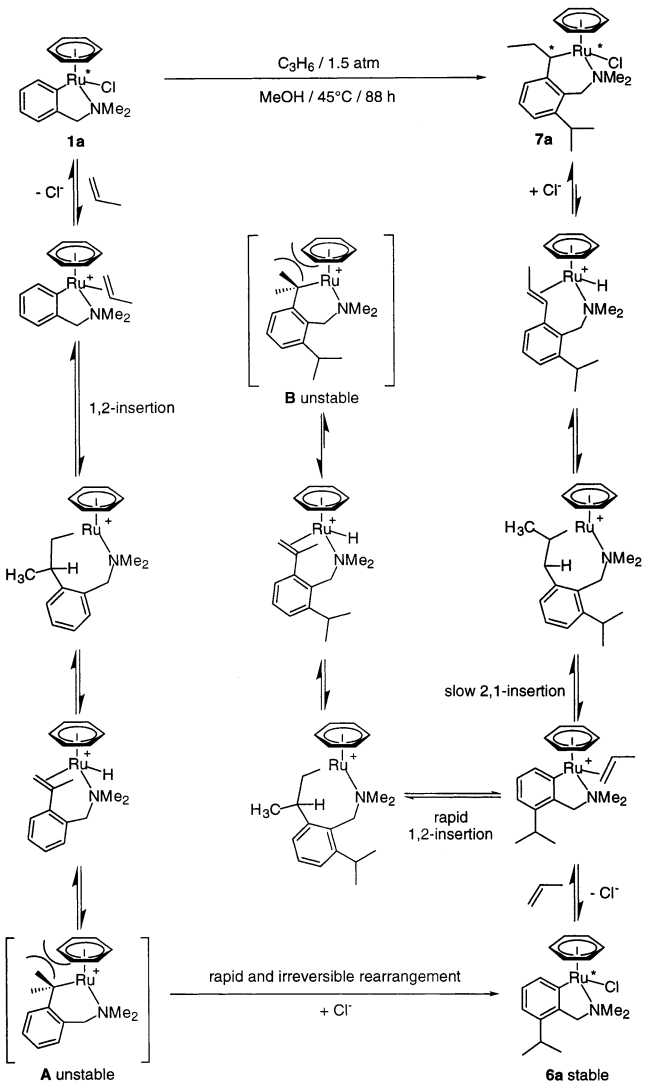
Conclusion

The reaction between terminal olefins and cycloruthenated tertiary amines was shown to be chemoselective, leading stoichiometrically either to the organic dimethyl((2-ethenylphenyl)methyl)amine and/or to an organometallic compound resulting from a formal one-carbon-atom insertion of the alkene into the Ru−C bond. This latter reaction proceeds stereospecifically and is without precedent in the field of the reactions between aryl−metal complexes and alkenes. It is most likely the strong directing effect of the CH_2NMe_2 group that prevents an easy decoordination of the product from the ruthenium center. Because of this behavior it is most

Scheme 4. Rearrangement Mechanism of the Six-Membered Metallacycle 3a



Scheme 5. Reaction Pathway for the Regiospecific Double Insertion of Propene on 1a



unlikely that any catalytic procedure might be observed with such N-containing substrates. This study has also shed light upon several important mechanistic effects, as it allowed us to establish the reversibility of most elementary steps of the formation of either the organic or the organometallic products of the reaction.

Experimental Section

All reactions were performed in Schlenk tubes under ethene or propene pressure. Further workup was always done under argon. Solvents were dried and distilled under argon prior to use: diethyl ether and *n*-hexane over sodium/benzophenone, dichloromethane and acetonitrile over calcium hydride, methanol and ethanol over magnesium.

NMR Spectra. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on FT-Bruker AC 200, AC 300, and ARX 500 spectrometers operating at 200.13, 300.13, and 500.14 MHz for ^{1}H and 50.30, 75.47, and 125.77 MHz for ^{13}C. The ^{2}H NMR spectrum was recorded on a FT-Bruker DPX 400 spectrometer operating at 61.42 MHz. 2D COSY, 2D ROESY, ^{1}H/^{13}C HSQC, and ^{1}H/^{13}C HMBC were performed on a FT-Bruker ARX 500 spectrometer. In the cases of **5a** and **7a**, the assignments of the ^{1}H and ^{13}C NMR signals were made with the aid of 2D COSY and 2D ROESY and of ^{1}H/^{13}C HSQC and ^{1}H/^{13}C HMBC, respectively. The chemical shifts are referenced to the residual solvent peaks. Chemical shifts (δ) and coupling constants (J) are expressed in ppm and Hz, respectively.

Elemental Analyses. These analyses were performed by the Service Central de Microanalise du CNRS, Strasbourg, France, and by the Service de Microanalise de l'Institut Charles Sadron, Strasbourg, France.

Reactants. Ethene and propene are 3.5 grade quality gases. Methanol for analysis was purchased from Carlo Erba. [Ru(η^6-C_6H_6){2-(CH_2NMe_2-κN)-C_6H_4-κC^1}]Cl (**1a**),[18] [Ru(η^6-C_6H_6){2-(CH_2NMe_2-κN)-C_6H_4-κC^1}NCMe]$^+PF_6^-$ (**1b**),[19] and [Ru(η^6-C_6H_6){2-(CH_2NMe_2-κN)-C_6H_4-κC^1}PMe_2Ph]$^+PF_6^-$ (**1c**)[13] were prepared according to published methods. Column chromatography was performed on Al_2O_3 (aluminum oxide 90, Merck).

Dimethyl((2-ethenylphenyl)methyl)amine (2). A suspension of **1a** (0.200 g, 0.57 mmol) in CH_3CN (25 mL) was stirred at room temperature under 1.5 bar of C_2H_4 for 24 h. The resulting suspension was filtered over Celite to remove elemental Ru. An aliquot of the solution was analyzed by ^{1}H NMR in $CDCl_3$, and signal integrations of the reaction product and **1a** indicated 50% conversion to **2**. The solution was then evaporated to dryness, and the resulting residue redissolved in methanol (1−2 mL). An orange solid was precipitated by addition of diethyl ether. Removal of the latter gave a pale yellow solution that was filtered over Al_2O_3 (4 × 2 cm) with diethyl ether as eluent. A colorless fraction was collected and concentrated in vacuo to give pure **2** as an oil (0.020 g, 22% yield).

2. ^{1}H NMR ($CDCl_3$, 200.13 MHz): δ 7.55 (m, 1H, C_6H_4), 7.26 (m, 3H, C_6H_4), 7.17 (dd, 1H, C*H*=CH_2, ^3J = 17.5, ^3J = 11.0), 5.68 (dd, 1H, CH=CH_EH$_Z$, ^3J = 17.5, ^2J = 1.4), 5.30 (dd, 1H, CH=CH_EH$_Z$, ^3J = 11.0, ^2J = 1.4), 3.44 (s, 2H, CH_2N), 2.24 (s, 6H, NMe_2).

[Ru(η^6-C_6H_6){1-(CHMe-κC)-2-(CH_2NMe_2-κN)-C_6H_4}Cl] (3a). An orange suspension of **1a** (0.080 g, 0.23 mmol) in methanol (15 mL) was stirred at room temperature under 1.5 atm of C_2H_4. The solid dissolved after 5 min, giving a red solution containing a very small amount of elemental Ru. After 1.5 h of reaction, an aliquot of the solution was removed by syringe, immediately dried in vacuo, and redissolved in $CDCl_3$. ^{1}H NMR indicated quasi-quantitative conversion to **3a**.[20] The red solution was then filtered over Celite to remove elemental Ru and concentrated in vacuo. The resulting residue was redissolved in CH_2Cl_2 (1−2 mL), and a red solid (0.080 g, 92% yield) precipitated after the addition of *n*-hexane.

3a. Anal. Calcd for $C_{17}H_{22}NClRu\cdot{}^1/_4CH_2Cl_2$ (the amount of CH_2Cl_2 was checked by ^{1}H NMR): C, 52.04; H, 5.70 N, 3.52. Found: C, 52.27; H, 5.72; N, 3.66. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ 7.58 (d, 1H, C_6H_4, ^3J = 7.7), 7.33 (m, 2H, C_6H_4), 6.88 (d, 1H, C_6H_4, ^3J = 4.0), 4.90 (s, 6H, C_6H_6), 3.53 (q, 1H, C*H*CH_3, ^3J = 7.1), 3.39 and 2.29 (AB, 2H, CH_2N, ^2J = 11.4), 3.24 and 2.28 (2s, 6H, NMe_2), 2.14 (d, 3H, CHC*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.47 MHz): δ 153.8, 133.3, 129.4, 129.0, 121.6, and 120.4 (C_6H_4), 83.0 (C_6H_6), 64.7 (CH_2N), 56.5 and 56.3 (NMe_2), 36.8 (CHRu), 24.5 (CH*C*H$_3$).

Reaction of 1a in Methanol-d_4: Deuterium-Labeling Experiment. To **1a** (0.075 g, 0.21 mmol) was added 5 mL of degassed CD_3OD. Pressurization of the resulting suspension with 1.5 atm of C_2H_4 led instantaneously to an orange-red suspension stirred for 1.5 h at room temperature. The solution was filtered over Celite to remove elemental Ru and concentrated in vacuo. The residue was then redissolved in CH_2Cl_2 (1−2 mL), and an orange solid (0.075 g, 92% yield) was precipitated by addition of *n*-hexane. ^{1}H and ^{2}H NMR showed equal incorporation of deuterium in **3a** at the asymmetric carbon and corresponding methyl levels.

(18) Abbenhuis, H. C. L.; Pfeffer, M.; Sutter, J. P.; de Cian, A.; Fischer, J.; Ji, L. H.; Nelson, J. H. *Organometallics* **1993**, *12*, 4464.

(19) Fernandez, S.; Pfeffer, M.; Ritleng, V.; Sirlin, C. *Organometallics* **1999**, *18*, 2390.

(20) The data reported in entry 1 of Table 1 have been obtained with a large selection of methanol batches; therefore, the value in Table 1 is an average value among many experiments.

3a-*d*. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ 7.58 (d, 1H, C_6H_4, ^3J = 7.8), 7.34 (m, 2H, C_6H_4), 6.88 (d, 1H, C_6H_4, ^3J = 3.9), 4.90 (s, 6H, C_6H_6), 3.51 (q and t, 0.5H, C*H*CH_3 and C*H*CH_2D, ^3J = 6.8), 3.39 and 2.30 (AB, 2H, CH_2N, ^2J = 11.2), 3.25 and 2.27 (2s, 6H, NMe_2), 2.14 (2d + 2s, 2.5H, CHC*H*$_3$, CDC*H*$_3$, CHC*H*$_2$D, and CDC*H*$_2$D, ^3J = 6.8). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.47 MHz): δ 153.6, 133.2, 129.2, 128.9, 121.5, and 120.3 (6s, C_6H_4), 82.9 (s, C_6H_6), 64.5 (s, CH_2N), 56.3 (s, NMe_2), 36.7 (s, CHRu), 24.4 (s, CH*C*H_3). ^{2}H NMR ($CHCl_3$, 61.42 MHz): δ 3.55 (bs, 1D, C*D*CH_3 and C*D*CH_2D), 2.18 (bs, 1D, $CHCH_2$*D* and $CDCH_2$*D*).

[Ru(η^6-C_6H_6){1-(CHMe-κ*C*)-2-(CH_2NMe_2-κ*N*)-C_6H_4}(NCMe)]$^+PF_6^-$ (3b). A yellow suspension of **1b** (0.100 g, 0.20 mmol) in methanol was stirred at room temperature under 1.5 atm of C_2H_4. The solid dissolved after 15 min, leading to a red solution. After 1.5 h of reaction, an aliquot of the solution was removed by syringe, filtered over Al_2O_3, immediately dried in vacuo, and redissolved in CD_3CN. ^{1}H NMR indicated 85% conversion to **3b** and 15% to **2**. The solution was then concentrated in vacuo. The resulting red residue was redissolved in CH_3CN (1−2 mL) and filtered over Al_2O_3 using CH_3CN as eluent. An orange fraction was collected and evaporated to dryness to give a red solid (0.060 g, 58% yield).

3b: Anal. Calcd for $C_{17}H_{22}NRuPF_6$: C, 41.98; H, 4.56; N, 2.88. Found: C, 41.07; H, 4.56; N. 2.82. ^{1}H NMR (CD_3CN, 200.13 MHz): δ 7.62 (d, 1H, C_6H_4, ^3J = 7.4), 7.34 (m, 2H, C_6H_4), 6.99 (d, 1H, C_6H_4, ^3J = 6.6), 5.14 (s, 6H, C_6H_6), 3.24 and 2.63 (AB, 2H, CH_2N, ^2J = 11.8), 3.09 (q, 1H, C*H*CH_3, ^3J = 7.4), 3.01 and 2.38 (2s, 6H, NMe_2), 2.14 (s, CH_3CN and H_2O), 2.08 (d, 3H, CHC*H*$_3$). ^{13}C{^{1}H} NMR (CD_3CN, 50.30 MHz): δ 130.5, 130.2, 129.4, 123.5, and 121.4 (C_6H_4), 118.3 (N*C*CH_3), 87.3 (C_6H_6), 65.4 (CH_2N), 57.8 and 57.0 (NMe_2), 34.0 (*C*HCH_3), 24.8 (CH*C*H_3), 1.3 (NC*C*H_3).

[Ru(η^6-C_6H_6){2-(CH_2NMe_2-κ*N*)-3-Et-C_6H_3-κ*C*^{1}}Cl] (4a). An orange suspension of **1a** (0.200 g, 0.57 mmol) in methanol (30 mL) was stirred at room temperature under 1.5 atm of C_2H_4. The solid dissolved after 5 min, leading to a red solution containing small amounts of elemental Ru. After 1.5 h of reaction, the solution was put under argon and stirred for 7 days at room temperature. The reaction medium gradually turned brown-red. After 3 days, an aliquot of the solution was removed by syringe and immediately dried in vacuo and the residue redissolved in $CDCl_3$. ^{1}H NMR signal integrations indicated 46% conversion to **3a** and 54% to **4a**. After 7 days, the same procedure showed complete conversion to **4a**, together with some decomposition. **4a** could not be isolated analytically pure but was identified by ^{1}H and ^{13}C{^{1}H} NMR.

4a. ^{1}H NMR ($CDCl_3$, 200.13 MHz): δ 8.03 (d, 1H, C_6H_3, ^3J = 7.4), 7.02 (t, 1H, C_6H_3), 6.74 (d, 1H, C_6H_3), 5.33 (s, 6H, C_6H_6), 4.20 (AB, 2H, CH_2N, ^2J = 13.0), 3.28 and 2.71 (2s, 6H, NMe_2), 2.41 (q, 2H, C*H*$_2$$CH_3$, ^3J = 7.5), 1.08 (t, 3H, CH_2C*H*$_3$). ^{13}C NMR ($CDCl_3$, 50.30 MHz): δ 166.7, 143.9, 138.3, 135.6, 126.1, and 123.3 (C_6H_3), 85.5 (C_6H_6), 68.3 (CH_2N), 58.3 and 55.6 (NMe_2), 27.7 (CH_2CH_3), 15.0 (CH_2CH_3).

[Ru(η^6-C_6H_6){1-(CHMe-κ*C*)-2-(CH_2NMe_2-κ*N*)-3-Et-C_6H_3}Cl] (5a). A suspension of **1a** (0.075 g, 0.21 mmol) in methanol (15 mL) was stirred at room temperature under 1.5 atm of C_2H_4 for 7 days. The solid dissolved after 5 min, leading to a red solution containing small amounts of elemental Ru. The reaction medium gradually turned brown-red. At the end of the reaction, the solution was filtered over Celite and evaporated to dryness. The resulting red residue was redissolved in CH_2Cl_2 (3 mL) and filtered over Al_2O_3 (10 × 3 cm). Elution with CH_2Cl_2 containing from 5% to 20% of methanol allowed collection of an orange fraction that was concentrated in vacuo to ca. 2 mL of solvent. Addition of *n*-hexane led to precipitation of a brown solid resulting from decomposition that was removed by filtration. The resulting yellow solution gave an orange solid (0.020 g, 24% yield) upon evaporation to dryness.

5a. Anal. Calcd for $C_{19}H_{26}NRuCl$: C, 56.36; H, 6.47; N, 3.46. Found: C, 54.96; H, 6.47; N. 3.35. ^{1}H NMR ($CDCl_3$, 500.14 MHz): δ 7.51 (d, 1H, H6, ^3J = 7.7), 7.28 (t, 1H, H5, ^3J = 7.7), 6.82 (d, 1H, H4, ^3J = 7.7), 4.90 (s, 6H, C_6H_6), 3.44 (q, 1H, C*H*CH_3, ^3J = 7.1), 3.29 and 2.34 (2s, 6H, NMe_2), 3.14 and 2.79 (AB, 2H, CH_2N, ^2J = 12.1), 2.71 and 2.51 (ABX, 2H, C*H*$_2$$CH_3$, ^2J = 14.7, ^3J = 7.5), 2.15 (d, 3H, CHC*H*$_3$, ^3J = 7.1), 1.12 (t, 3H, CH_2C*H*$_3$, ^3J = 7.5). ^{13}C{^{1}H} NMR ($CDCl_3$, 125.77 MHz): 128.5 (C5), 122.1 (C4), 118.9 (C6), 83.0 (C_6H_6), 57.6 (CH_2N), 56.9 and 55.7 (NMe_2), 37.6 (*C*HCH_3), 26.2 (*C*H_2CH_3), 25.2 (CH*C*H_3), 15.9 (CH_2CH_3).

[Ru(η^6-C_6H_6){2-(CH_2NMe_2-κ*N*)-3-*i*Pr-C_6H_3-κ*C*^{1}}Cl] (6a) and [Ru(η^6-C_6H_6){1-(CHEt-κ*C*)-2-(CH_2NMe_2-κ*N*)-3-*i*Pr-C_6H_3}Cl] (7a). An orange suspension of **1a** (0.095 g, 0.27 mmol) in methanol was stirred at 45 °C under 1.5 atm of C_3H_6 over 88 h. The solid dissolved after 1.5 h, leading to a red-orange solution with a small amount of elemental Ru. After 3 and 6 h of reaction, an aliquot of the solution was removed by syringe and immediately dried in vacuo and the residue redissolved in $CDCl_3$. ^{1}H NMR signal integrations indicated respectively 40% and 70% conversion to a new complex, assumed to be **6a**. After 23 h, the same procedure showed 48% of **6a** and 52% of **7a**. After 52 h, 17% of **6a** and 83% of **7a** were observed, and after 88 h, the reaction was almost complete (more than 95% of **7a**). The solution was then evaporated to dryness. The resulting red residue was redissolved in CH_2Cl_2 (2 mL) and the solution subjected to column chromatography on Al_2O_3 (10 × 3 cm). Elution with CH_2Cl_2 containing from 2% to 15% of methanol allowed collection of an orange fraction that was concentrated in vacuo. The red residue was redissolved in CH_2Cl_2 (1 mL), and a brown solid resulting from decomposition precipitated after addition of *n*-hexane. Filtration of the latter gave an orange solution that was evaporated to dryness. The orange solid was not pure and has been identified by 2D COSY, 2D ROESY, ^{1}H/^{13}C HSQC, and ^{1}H/^{13}C HMBC.

6a. ^{1}H NMR ($CDCl_3$, 200.13 MHz): 8.03 (dd, 1H, C_6H_3, ^3J = 7.4, ^4J = 1.2), 7.06 (t, 1H, C_6H_3), 6.85 (dd, 1H, C_6H_3), 5.33 (s, 6H, C_6H_6), 4.22 and 3.12 (AB, 2H, CH_2N, ^2J = 13.0), 3.28 and 2.71 (2s, 6H, NMe_2), 1.15 and 1.10 (2d, 6H, $CH(CH_3)_2$, ^3J = 6.9).

7a. ^{1}H NMR ($CDCl_3$, 263 K, 500.14 MHz): 7.48 (d, 1H, H_6, ^3J = 7.6), 7.29 (t, 1H, H_5), 6.87 (d), 3.06 and 2.88 (AB, 2H, CH_2N, ^2J = 12.2), 3.18 (dd, 1H, C*H*CH_2CH_3, ^3J = 10.8 and ^3J = 4.0), 3.01 (m, 2H, CHC*H*$_2$$CH_3$, ^3J not resolved), 1.22 (d, 3H, CH(C*H*$_3$)), 1.07 (d, 3H, CH(C*H*$_3$)), 1.02 (t, 3H, $CHCH_2CH_3$, ^3J = 7.1). ^{13}C{^{1}H} NMR (CD_3CN, 125.77 MHz): δ 151.7 (C1), 146.1 (C3), 130.0 (C2), 128.1 (C5), 118.3 (C6 and C4), 83.0 (C_6H_6), 56.5 (CH_2N), 56.5 and 55.8 (NMe_2), 47.1 ($CHCH_2CH_3$), 32.0 ($CHCH_2CH_3$), 28.8 ($CH(CH_3)_2$), 25.8 (CH(*C*H_3)), 22.5 (CH(*C*H_3)), 16.4 ($CHCH_2CH_3$).

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Note Added after ASAP: The version of the paper published on the Web 12/20/2002 had text inadvertently switched on the second page, in the paragraphs Preliminary Observations and Reaction in CH_3CN. The final Web version published 1/3/2003 and the print version are correct.

Supporting Information Available: Text giving a detailed analysis of the 2D NMR spectra to establish the absolute configurations of the complexes **3a**, **5a**, and **7a** and the signal shape analysis of the deuterated compound of **3a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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