An Effective Route to Cycloruthenated N-Ligands under Mild Conditions

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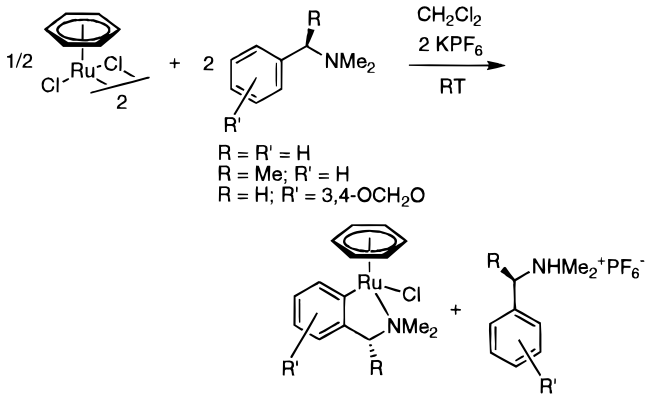
Received February 17, 1999

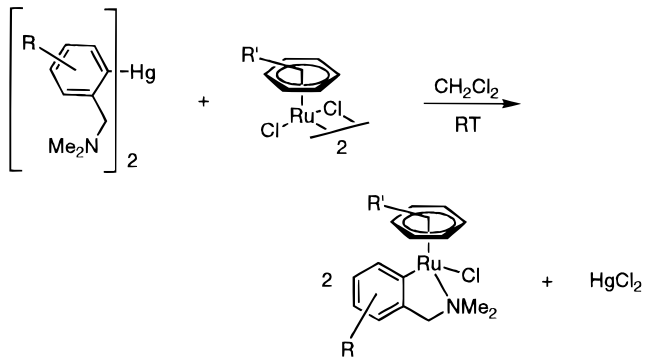
Summary: Cycloruthenated complexes of the type [(η^6-C_6H_6)Ru(C∧N)CH_3CN]$^+PF_6^-$ (C∧N = C_6H_4-2-CH_2NMe_2, (R)-(+)-C_6H_4-2-CH(Me)NMe_2, C_6H_2-3,4-$(OCH_3)_2$-2-CH_2-NMe_2) are readily obtained by the intramolecular C−H activation of N,N-dimethylbenzylamine derivatives with [(η^6-C_6H_6)$RuCl_2$]$_2$ in up to 53% isolated yields. Under similar conditions, 8-methylquinoline also led to a cycloruthenated complex, though in lower yield (12%) and after a longer reaction time. Reaction with the optically active (R)-(+)-N,N-dimethyl-1-phenylethylamine led to a 48% diastereomeric excess in the cycloruthenated product. Under the same conditions, and after 14 and 65 h of reaction time, respectively, 2-phenyl- and 2-benzylpyridine are cyclometalated, leading to the formation of complexes in which the benzene ligand has been substituted by three acetonitriles: [(C∧N)Ru(CH_3CN)$_4$]$^+$-PF_6^- (C∧N = C_6H_4-2-C_5H_4N, C_6H_4-2-(CH_2)-C_5H_4N) were obtained in 40 and 24% isolated yields, respectively.

Introduction

During our search to define useful applications of intramolecular C−H activation processes involving transition metals, we recently discovered that ruthenium(II) derivatives could efficiently complement their widely used palladium(II) congeners.[1] Indeed, cycloruthenated *N,N*-dimethylbenzylamines have been shown to lead to heterocyclic products in a one-pot procedure through reaction with internal alkynes.[2] Moreover, since its applicability accommodated a larger selection of alkynes than with palladium, the scope of this reaction proved to be wider in the case of ruthenium derivatives. However, one setback is the relative lack of reactivity of ruthenium complexes toward the cyclometalation reaction. Previous attempts to cycloruthenate substituted *N,N*-dimethylbenzylamines did not run satisfactorily, as we could only achieve this in three cases with unsatisfactory yields (i.e. *N,N*-dimethylbenzylamine, the corresponding 3,4-dioxymethylene derivative, and (*R*)-*N,N*-dimethyl-1-phenylethylamine) (eq 1).[2a]



Consequently, these organoruthenium compounds were prepared by transmetalation reactions, which was rather frustrating, since these required the use of mercury derivatives of *N,N*-dimethylbenzylamines (eq 2).[2a,3]



We have thus reinvestigated this elementary step, as its solution would enable us to have better chances of investigating the ruthenium-catalyzed functionalization of C−H bonds. We now describe in this paper an improved method for effecting the cycloruthenation of N-containing ligands.

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10.1021/om9901067 CCC: $18.00
Publication on Web 05/14/1999

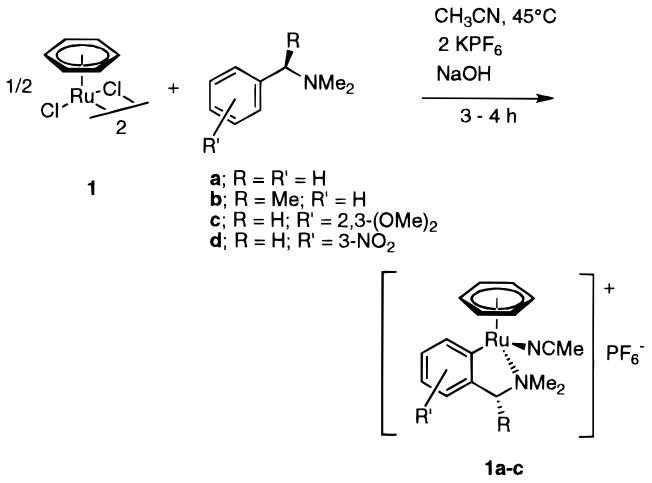
Table 1. Reactions of 1 with N-Containing Ligands (a−g)

ligand	product	reacn time (h)[a]	conversn (%) in soln[b]	yield (%)[c]	product ratio[b]
a	**1a**	3	60	50	
b	**1b/1b′**	4	51	49	3/1
c	**1c**	3	71	53	
d		18	0	0	
e	**1e**	24	18	12	
f	**1f/2f**	3	27	/	1/3
		14	43	40	0/1
g	**1g/2g**	18	70	/	1/1
		65	54[d]	24	0/1

[a] Reactions performed in CH_3CN at 45 °C except in the case of ligand **d** (room temperature). [b] Deduced from ^1H NMR signal integrations of the reaction products and N ligands. [c] Isolated yields. [d] See ref 8.

Results

During our quest to optimize the cycloruthenation reaction, we observed that the substitution of a chloro ligand by acetonitrile led to cationic cycloruthenated complexes which were less prone to oxidation by traces of oxygen. Indeed, these cationic complexes are stable in solution under nitrogen for at least 24 h, whereas they are air-stable for a few hours as solids. Consequently, we chose to run the reactions in acetonitrile. In a typical experiment a suspension of $[(\eta^6\text{-}C_6H_6)\text{-}RuCl_2]_2$ **1** (1 equiv), *N*,*N*-dimethylbenzylamine (2 equiv), NaOH (2 equiv), and KPF_6 (4 equiv) was stirred for 3−4 h at 45 °C in CH_3CN (eq 3). It is noteworthy that under

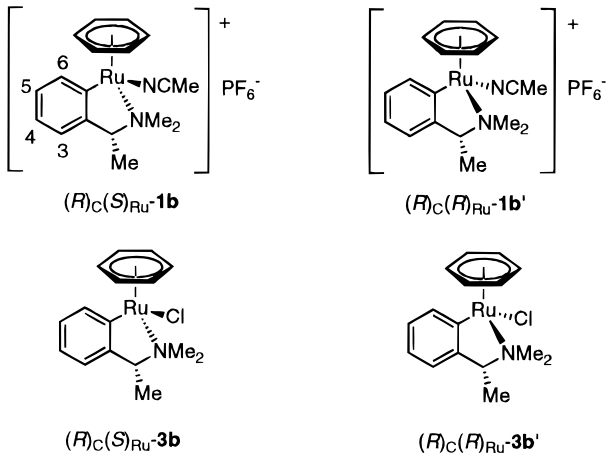


these conditions the cycloruthenation reaction could be achieved with only 1 equiv of ligand per ruthenium instead of 2 equiv as in previous reactions, a feature which is particularly appreciable in the case of chiral amines such as **b**, which are often expensive.

Ligands **a** and **c** reacted with **1** to give the expected cycloruthenated compounds **1a** and **1c**, respectively, in good yields, whereas no reaction occurred with ligand **d** (eq 3 and Table 1). **1a** and **1c** were identified by ^1H NMR and elemental analyses.

The reaction of **1** with enantiomerically pure $(R)_C\text{-}C_6H_5CH(CH_3)NMe_2$ (**b**) resulted in an overall conversion of 51% for the two diastereomeric ruthenacycles **1b** and **1b′** after 4 h of reaction. Filtration over Al_2O_3 using CH_3CN as eluant gave only one fraction, from which an orange solid was obtained in 49% yield. Both diastereomers were still present in the same ratio (Table 1).

Chart 1



From their integrated intensities (74% for **1b** and 26% for **1b′**) a diastereomeric excess (de) of 48% for **1b** was calculated. The two obtained diastereomers show well-separated signals in their ^1H NMR spectrum (CD_3CN) (Table 2). Therefore, comparison of the latter spectrum with that of the chlorinated derivatives $(R)_C,(S)_{Ru}$-**3b** and $(R)_C,(R)_{Ru}$-**3b′**[3b] ($CDCl_3$) (Chart 1 and Table 2) allowed us to identify **1b** and **1b′** as the acetonitrile monocationic analogues of **3b** and **3b′**, respectively, and then to assign to the former the structures shown in Chart 1. The chemical shift of the H2 protons, ortho to the Ru−C bond, seems to be the most diagnostic for the structure elucidation of the complexes. In **1b** and **3b**, for instance, they are both found at ca. 8.2 ppm, i.e., significantly deshielded (by ca. 0.5 ppm) compared to the corresponding protons in **1b′** and **3b′**. Since the chiral benzylic carbon atom of **b** is not a reaction center during the formation of this pair of diastereomers, its absolute configuration ($(R)_C$) remains fixed. The absolute configuration at ruthenium is assigned assuming the following priority numbers:[4] 1 ($\eta^6\text{-}C_6H_6$), 2 (NCMe), 3 (NMe_2), and 4 (phenyl C atom). Thus, **1b** is designated as the $(R)_C,(S)_{Ru}$ diastereomer and **1b′** as the $(R)_C,(R)_{Ru}$ diastereomer.

With the goal of extending this cycloruthenation protocol to other systems, we reacted N-ligands for which cyclopalladated and/or cycloruthenated analogues were already known, i.e., 8-methylquinoline (**e**),[5] 2-phenylpyridine (**f**),[6] and 2-benzylpyridine (**g**)[7] (Chart 2).

Reaction of **1** with **e** under the conditions described above led to only 2% conversion to the expected cycloruthenated species **1e** after 3 h, but 18% conversion was observed after 24 h to give a 12% yield of **1e** after workup. Cyclometalation conversions observed with **f** and **g** were rather high, but a drastic change occurred in the nature of the obtained cycloruthenated species. Indeed, we observed the formation of the unexpected cycloruthenated complexes **2f** and **2g,** in which the benzene unit had been substituted by three acetonitrile ligands (Chart 2). ^1H NMR spectroscopy and elemental analyses confirmed the proposed formula. In the case

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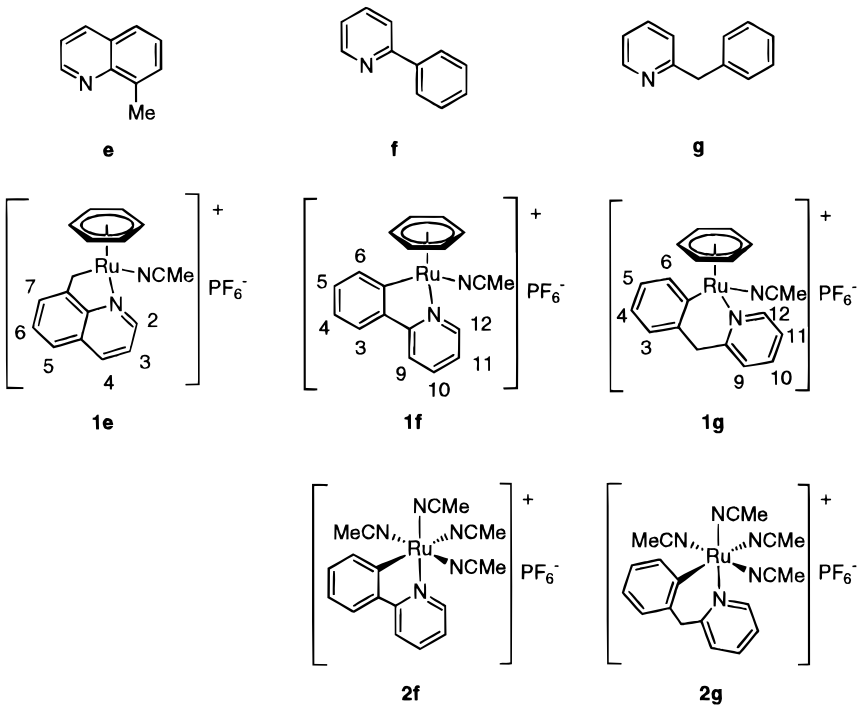
(7) Hiraki, K.; Fuchita, Y.; Takechi, K. *Inorg. Chem.* **1981**, *20*, 4316.

Table 2. ^{1}H NMR Data (δ in ppm and J in Hz) of Cycloruthenated (*R*)-*N*,*N*-Dimethyl-1-phenylethylamine

	^{1}H chem shift				
product	aromatics[a]	η^6-C_6H_6	$CHCH_3$	NMe_2	CH_3CN[d]
1b[b]	8.15 (dd, 1H, H6, ^3J = 7.3, ^4J = 1.2) 7.09 (t, 1H, H5) 7.01 (t, 1H, H4) 6.87 (d, 1H, H3)	5.66 (s, 6H)	3.70 (q, 1H, CH, ^3J = 6.8) 1.23 (d, 3H, CH_3)	3.17 and 2.46 (2s, 6H)	2.13 s
3b[c,e]	8.24 (dd, 1H, H6, ^3J = 7.5, ^4J = 1.5) 7.08 (t, 1H, H5) 6.95 (t, 1H, H4) 6.77 (d, 1H, H3)	5.34 (s, 6H)	4.37 (q, 1H, CH, ^3J = 7.0) 1.18 (d, 3H, CH_3)	3.38 and 2.47 (2s, 6H)	
1b′[b]	7.67 (dd, 1H, H6, ^3J = 7.3, ^4J = 1.2) 7.09 (t, 1H, H5) 7.02 (t, 1H, H4) 6.83 (d, 1H, H3)	5.57 (s, 6H)	3.94 (q, 1H, CH, ^3J = 6.8) 1.27 (d, 3H, CH_3)	3.32 and 2.15 (2s, 6H)	2.13 s
3b′[c,e]	7.75 (dd, 1H, H6, ^3J = 7.5, ^4J = 1.5) 7.11 (t, 1H, H5) 6.94 (t, 1H, H4) 6.74 (d, 1H, H3)	5.29 (s, 6H)	3.83 (q, 1H, CH, ^3J = 7.0) 1.28 (d, 3H, CH_3)	3.36 and 1.96 (2s, 6H)	

[a] The numbering of the aryl protons follows that depicted in Chart 1. [b] Spectra measured in CD_3CN. [c] Spectra measured in $CDCl_3$. [d] The CH_3CN singlets do not integrate for the expected number of protons due to the CD_3CN/CH_3CN exchange process. [e] See ref 3b.

Chart 2



of **f** after 3 h of reaction, 27% conversion of complex **1** was observed, leading to a 1:3 mixture of **1f** and **2f**. After 14 h all of **1f** had reacted and **2f** was the only product observed. It was isolated in 40% yield after workup. Reaction of **1** with **g** gave an overall conversion of 70% after 18 h of reaction, leading to a 1:1 mixture of **1g** and **2g**. After 65 h **1g** had almost completely reacted (1% remaining) and the conversion to **2g** had risen to 53%.[8] **2g** was then isolated in 24% yield after workup (Table 1).

Discussion

These results allow us to make several observations. The absence of reactivity for ligand **d**, which is substituted by a strongly withdrawing substituent, compared to a high conversion to the expected complex observed for ligand **c**, militates in favor of a strong electronic effect on the reaction course. Such a chemoselectivity appears to indicate that cycloruthenation by C−H activation occurs via an aromatic electrophilic substitution in which ruthenium is the electrophilic center: i.e., akin to palladium-mediated cyclometalations.[9] These results confirm what was already thought when the reaction was carried out under eq 1 conditions: the reaction of **1** and an arylamine containing a dioxymethylene unit gave the best yield.[2a]

(8) Running the reaction for a longer time did not improve the conversion to **2g**. *A contrario,* another compound containing a coordinated or activated 2-benzylpyridine unit was detected by ^{1}H NMR spectroscopy after 65 h reaction. Sixteen percent conversion to this product (with respect to the amount of 2-benzylpyridine used) was observed, but it could never be isolated and thus has not been identified up to now. It is noteworthy that separation of **2g** from this latter compound was difficult. This explains the important loss of product observed when comparing the yield obtained and the conversion in solution.

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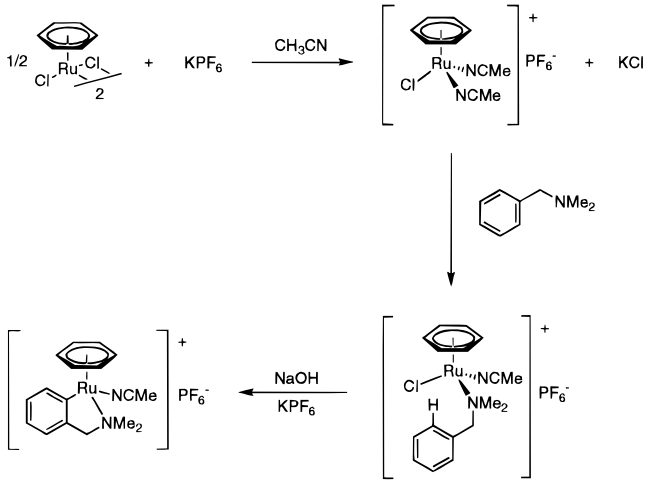
It is worth mentioning the important loss of diastereoselectivity observed when comparing the transmetalation reaction of enantiomerically pure $(R)_C$-[HgCl($C_6H_4CH(Me)NMe_2$)] with **1**, where the de was 90%,[3b] and the direct C−H activation process described here. We have checked that performing the reaction in the absence of NaOH but with another equivalent of the optically active tertiary amine did not improve the process, as the de was 52% whereas the conversion dropped to 21%, this indicating that the stereoselectivity of the C−H activation process is not controlled by the nature of the base used.[18] Trying to draw conclusions related to the reaction mechanism from these different stereoselectivities would appear very speculative, as the genuine mechanism of the intramolecular C−H activation is far from being well understood (several different intermediates have been proposed for this reaction[10]). Hence, this result deserves a detailed mechanistic and/or theoretical investigation, which is outside the scope of the present study.

Good yields of cycloruthenated compounds are obtained in this work, as compared to the results obtained previously.[2a] A recent study[11] showed that [(η^6-C_6H_6)-$RuCl(CH_3CN)_2]^+X^-$ complexes could be easily obtained by reaction of **1** with 1 equiv of $TlPF_6$, NH_4PF_6, $LiBF_4$, or $KAsF_6$ per ruthenium in acetonitrile. Moreover, the lability of the acetonitrile ligands has also been evidenced by a fast CD_3CN/CH_3CN exchange, which was detected in the ^1H NMR spectra of [(η^6-C_6H_6)$RuCl(CH_3CN)_2]^+BF_4^-$, and by their substitution by ligands such as 1,2-bis(diphenylphosphino)benzene, 2,2′-bipyridine, and 1,10-phenanthroline. Thus, in our case, the enhancement of reactivity observed in CH_3CN may be explained by the formation of an [(η^6-C_6H_6)$RuCl(CH_3CN)_2]^+PF_6^-$ intermediate as the reactive species. To support this hypothesis, we ran the reaction by starting with this latter ruthenium complex along with **a** and NaOH in CD_3CN in an NMR tube. This led to a 67% conversion to **1a** after 1 day. This result allows us to propose a reaction pathway in which N-coordination and the electrophilic steps may be much easier and faster than when the reaction was performed in CH_2Cl_2 (Scheme 1).

Arene displacement by three acetonitrile ligands during the cycloruthenation of ligands **f** and **g** was unexpected, since it did not occur in the case of *N*,*N*-dimethylbenzylamine derivatives even when reactions were carried out for 1 day. Bennett and Smith,[12a] as well as Zelonka and Baird,[12b,c] reported that (η^6-arene)$RuCl_2$-(PR_3) complexes undergo partial or complete arene exchange on heating (110 °C < *T* < 170 °C) or on UV irradiation in an aromatic solvent. They also reported that an excess of ligand should be avoided in the preparation of (η^6-arene)$RuCl_2(PR_3)$ complexes from **1**, since otherwise the coordinated arene may be displaced. Weber and Ford[12d] also described the arene photosubstitution of [(η^6-arene)$RuL_3]^{2+}$ (L = NH_3, H_2O) complexes in aqueous solution. Analogous mechanisms have been proposed for thermal and photo displacement of coordinated arenes.[12d,13] They are based on the weakening of the metal−arene bond. Thus, in the case of photosubstitution, the excited state would have a distorted metal−arene bond which would then react with the solvent. This suggests that a reasonable explanation for the cycloruthenation of **f** and **g** would be related to the stronger coordinating character of pyridines, which would weaken the benzene−ruthenium bond, thus allowing benzene displacement by acetonitrile.

Scheme 1



Conclusion

The results reported here are interesting, since they allow us to prepare organoruthenium compounds by direct intramolecular C−H activation. It is noteworthy that now even an aliphatic C−H unit may be activated and that the cycloruthenation of ortho-substituted aryl groups can be achieved with much better yields than those reported before. This improves the potential of ruthenium-catalyzed functionalization of C−H bonds. Studies in this direction are currently under way.

Experimental Section

All reactions were performed in Schlenk tubes under nitrogen unless otherwise specified. Solvents were dried and distilled under nitrogen prior to use: diethyl ether and *n*-hexane over sodium/benzophenone, dichloromethane and acetonitrile over calcium hydride. The ^1H NMR spectra were recorded at 200.13 or 300.13 MHz on FT-Bruker SY200 and AM300 spectrometers and referenced to solvent signals. Column chromatography was performed under nitrogen using Al_2O_3 as support (alumina 90, Merck). Elemental analyses were performed by the Service Central de Microanalyze du CNRS, Strasbourg, France, and by the Service de Microanalyze du Centre de Recherche sur les Macromolécules, Strasbourg, France. Commercial compounds were used as received. [(η^6-C_6H_6)$RuCl_2]_2$ (**1**),[12b] [(η^6-C_6H_6)$RuCl(CH_3CN)_2]^+PF_6^-$,[11] and substituted *N*,*N*-dimethylbenzylamines[14] were prepared according to published methods.

[(η^6-C_6H_6)Ru(C_6H_4-2-CH_2NMe_2)(CH_3CN)]$^+PF_6^-$ (1a). Route 1. A suspension of [(η^6-C_6H_6)$RuCl_2]_2$ (**1**; 0.200 g, 0.4 mmol), *N*,*N*-dimethylbenzylamine (**a**; 0.120 mL, 0.8 mmol), NaOH (0.031 g, 0.8 mmol), and KPF_6 (0.292 g, 1.6 mmol) in CH_3CN

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(5 mL) was stirred at 45 °C for 3 h. The resulting dark yellow suspension was filtered over Al_2O_3 (12 × 3 cm) using CH_3CN as eluant. A yellow fraction was collected and concentrated in vacuo. The resulting residue was redissolved in a minimum of CH_3CN (2 mL), and a yellow solid (0.200 g, 50% yield) precipitated after the addition of diethyl ether. Anal. Calcd for $C_{17}H_{21}N_2RuPF_6$: C, 40.83; H, 4.43; N, 5.60. Found: C, 40.81; H, 4.30; N, 5.61. ^{1}H NMR (300.13 MHz, CD_3CN): δ 8.06 (d, 1H, H6,[15] ^3J = 7.6 Hz), 7.00 (m, 3H, Ar), 5.64 (s, 6H, C_6H_6), 3.71 and 3.29 (AB, 2H, CH_2N, ^2J = 13.7 Hz), 2.98 and 2.73 (2s, 6H, NMe_2), 2.15 (s, CH_3CN[16]).

Route 2. The following reaction was performed in an NMR tube. To a yellow solution of $[(\eta^6\text{-}C_6H_6)RuCl(CH_3CN)_2]^+PF_6^-$ (0.020 g, 0.045 mmol) in CD_3CN was added *N*,*N*-dimethylbenzylamine (**a**; 6.7 μL, 0.045 mmol); the color of the solution turned instantaneously to orange. NaOH (0.002 g, 0.05 mmol) was then added, leading to a suspension. After 1 day ^{1}H NMR signal integrations of the reaction product and **a** indicated 67% conversion to **1a**.

$[(\eta^6\text{-}C_6H_6)Ru(C_6H_4\text{-}2\text{-}(R)\text{-}CH(Me)NMe_2)(CH_3CN)]^+PF_6^-$ (1b and 1b′). The procedure was the same as for **1a**: **1** (0.200 g, 0.4 mmol) and **b** (0.131 mL, 0.8 mmol) gave **1b** and **1b′** after 4 h of reaction (0.200 g, 49% yield). **1b** and **1b′** could not be separated by column chromatography. A de of 48% was deduced from ^{1}H NMR signal integrations. Anal. Calcd for $C_{18}H_{23}N_2RuPF_6$: C, 42.10; H, 4.51; N, 5.46. Found: C, 42.31; H, 4.58; N, 5.49. ^{1}H NMR data: see Table 2.

$[(\eta^6\text{-}C_6H_6)Ru(C_6H_2\text{-}3,4\text{-}(OCH_3)_2\text{-}2\text{-}CH_2NMe_2)(CH_3CN)]^+PF_6^-$ (1c). The same procedure as for **1a** was followed: **1** (0.200 g, 0.4 mmol) and **c** (0.156 mL, 0.8 mmol) gave **1c** (0.236 g, 53% yield). Anal. Calcd for $C_{19}H_{25}O_2N_2RuPF_6$: C, 40.79; H, 4.50; N, 5.01. Found: C, 41.02; H, 4.44; N, 5.07. ^{1}H NMR (CD_3CN, 300.13 MHz): δ 7.71 (d, 1H, H6, ^3J = 8.0 Hz), 6.79 (d, 1H, H5, ^3J = 8.0 Hz), 5.61 (s, 6H, C_6H_6), 3.62 and 3.58 (AB, 2H, CH_2N, ^2J = 14.1 Hz), 3.02 and 2.71 (2s, 6H, NMe_2), 3.79 and 3.64 (2s, 6H, OMe), 2.16 (s, CH_3CN).

$[(\eta^6\text{-}C_6H_6)Ru(8\text{-}CH_2C_9H_6N)(CH_3CN)]^+PF_6^-$ (1e). A suspension of $((\eta^6\text{-}C_6H_6)RuCl_2)_2$ (**1**; 0.200 g, 0.4 mmol), 8-methylquinoline (**e**; 0.114 g, 0.8 mmol), NaOH (0.031 g, 0.8 mmol), and KPF_6 (0.292 g, 1.6 mmol) in CH_3CN (5 mL) was stirred at 45 °C for 24 h. After 3 h an aliquot of the reaction mixture was removed by syringe, immediately concentrated in vacuo, and redissolved in CD_3CN for ^{1}H NMR measurement. ^{1}H NMR signal integrations of the reaction product and **e** indicated 2% conversion to **1e**. After 24 h the same procedure showed 18% conversion to **1e**. The resulting dark yellow suspension was filtered over Al_2O_3 using CH_2Cl_2/CH_3CN (3%) as eluant. A yellow fraction was collected and was concentrated in vacuo. The resulting residue was redissolved in CH_2Cl_2 (2 mL), and a yellow solid (0.050 g, 12% yield) was precipitated by the addition of diethyl ether and *n*-hexane. Anal. Calcd for $C_{18}H_{17}N_2RuPF_6$: C, 42.61; H, 3.38; N, 5.52. Found: C, 42.63; H, 3.30; N, 5.65. ^{1}H NMR (CD_3CN, 300.13 MHz): δ 9.53 (dd, 1H, H2, ^3J = 5.1 Hz, ^4J = 1.5 Hz), 8.36 (dd, 1H, H4, ^3J = 8.3 Hz, ^4J = 1.5 Hz), 7.71 (dd, 1H, H5, ^3J = 7.1 Hz, ^4J = 1.5 Hz), 7.66 (d, 1H, H7, ^3J = 8.0 Hz), 7.54 (dd, 1H, H6, ^3J = 7.1 Hz, ^3J = 8.0 Hz), 7.49 (dd, 1H, H3, ^3J = 5.1 Hz, ^3J = 8.3 Hz), 5.61 (s, 6H, C_6H_6), 5.02 and 3.15 (AB, 2H, CH_2, ^2J = 22.3 Hz), 2.15 (s, CH_3CN).

$[(C_6H_4\text{-}2\text{-}C_5H_4N)Ru(CH_3CN)_4)]^+PF_6^-$ (2f). A suspension of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ (**1**; 0.100 g, 0.2 mmol), 2-phenylpyridine (**f**; 0.057 mL, 0.4 mmol), NaOH (0.015 g, 0.4 mmol), and KPF_6 (0.146 g, 0.8 mmol) in CH_3CN (5 mL) was stirred at 45 °C for 14 h. After 3 h an aliquot of the reaction mixture was removed by syringe, immediately dried in vacuo, and redissolved in CD_3CN for ^{1}H NMR measurement. ^{1}H NMR signal integrations of reaction products and **f** indicated 6% conversion to **1f** and 21% to **2f**. After 14 h the same procedure showed 43% conversion to **2f** exclusively. The same workup as for **1e** then gave a yellow solid (0.091 g, 40% yield). Anal. Calcd for $C_{19}H_{20}N_5RuPF_6$: C, 40.43; H, 3.57; N, 12.41. Found: C, 41.43; H, 3.84; N, 12.30. ^{1}H NMR (CD_3CN, 300.13 MHz): δ 8.89 (ddd, 1H, H12, ^3J = 8.5 Hz, ^4J = 2.2 Hz, ^5J = 1.1 Hz), 7.95 (dd, 1H, H6 or H3, ^3J = 11.1 Hz, ^4J = 1.8 Hz), 7.86 (d, 1H, H9, ^3J = 11.8 Hz), 7.72 (ddd, 1H, H10, ^3J = 11.8 Hz, ^3J = 11.0 Hz n.r.,[17] ^4J = 2.2 Hz), 7.70 (dd, 1H, H3 or H6, ^3J = 11.1 Hz, ^4J = 2.2 Hz), 7.13 (ddd, 1H, H11, ^3J = 11.0 Hz, ^3J = 8.5 Hz, ^4J = 2.2 Hz), 7.06 (td, 1H, H5 or H4, ^3J = 11.1 Hz, ^4J = 2.2 Hz), 6.92 (td, 1H, H4 or H5, ^3J = 11.1 Hz, ^4J = 1.8 Hz), 2.51, 2.17 and 2.00 (3s, CH_3CN).

$[(C_6H_4\text{-}2\text{-}CH_2\text{-}C_5H_4N)Ru(CH_3CN)_4]^+PF_6^-$ (2g). A suspension of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ (**1**; 0.200 g, 0.4 mmol), 2-benzylpyridine (**g**; 0.135 g, 0.8 mmol), NaOH (0.031 g, 0.8 mmol), and KPF_6 (0.292 g, 1.6 mmol) was stirred in CH_3CN (5 mL) at 45 °C for 65 h. After 18 h an aliquot of the reaction mixture was removed by syringe, immediately dried in vacuo, and redissolved in CD_3CN for ^{1}H NMR measurement. ^{1}H NMR signal integrations of reaction products and **g** indicated 36% conversion to **1g** and 34% conversion to **2g**. After 65 h the same procedure showed 1% conversion to **1g** and 53% conversion to **2g**.[8] The same workup as for **1a** then gave a yellow solid (0.110 g, 24% yield). Anal. Calcd for $C_{20}H_{22}N_5RuPF_6$: C, 41.53; H, 3.83; N, 12.11. Found: C, 41.64; H, 3.69; N, 11.64. ^{1}H NMR (CD_3CN, 300.13 MHz): δ 8.83 (dd, 1H, H12, ^3J = 5.8 Hz, ^4J = 1.5 Hz), 7.68 (td, 1H, H10, ^3J = 7.6 Hz, ^4J = 1.5 Hz), 7.59 (dd, 1H, H9, ^3J = 7.6 Hz, ^4J = 1.5 Hz), 7.38 (dd, 1H, H6 or H3, ^3J = 7.3 Hz, ^4J = 1.5 Hz), 7.14 (ddd, 1H, H11, ^3J = 5.6 Hz, ^3J = 7.6 Hz, ^4J = 1.5 Hz), 6.99 (dd, 1H, H3 or H6, ^3J = 7.3 Hz, ^4J = 1.7 Hz), 6.88 (td, 1H, H5 or H4, ^3J = 7.3 Hz, ^4J = 1.7 Hz), 6.77 (td, 1H, H4 or H5, ^3J = 7.3 Hz, ^4J = 1.5 Hz), 4.23 (s, 2H, CH_2), 2.45, 2.21, and 2.16 (3s, CH_3CN).

Acknowledgment. Financial support of this work by the Ministère de l'Education Nationale, de la Recherche et de la Technologie (fellowship for V.R.) and the CSIC (Consejo superior de Investigaciones Cientificas) (fellowship for S.F.) are gratefully acknowledged.

OM9901067

(15) The numbering of the aryl protons follows that depicted in Charts 1 and 2.

(16) The CH_3CN singlet(s) do not integrate for the expected number of protons due to the CD_3CN/CH_3CN exchange process.

(17) n.r. = not resolved due to partial overlap of other protons.

(18) **Note Added in Proof.** The ^{1}H NMR spectrum of **3b** in CD_3CN revealed a mixture of **3b** together with a cationic derivative analogous to **1b** in which Cl^- is the counteranion instead of PF_6^- and whose de is exactly the same as that of **1b** (ca. 50%). This is a reversible process, as after removal of the CD_3CN in vacuo, a spectrum of $CDCl_3$ revealed again the same resonances as for **3b** with the same de (90%). Thus, the observed de for **1b** in acetonitrile is more likely to be the result of the stereoselectivity of the coordination of CH_3CN to the Ru center, as observed recently by Nelson et al., rather than reflecting the stereoselectivity of the C−H activation process. (See: Attar, S.; Catalano, V. J.; Nelson, J. H. *Organometallics* **1996**, *15*, 2932.