Ruthenium Carbene Complexes Containing a Triazolidene Cationic Ligand

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Received August 3, 2001

Reaction of the bis(dihydrogen)ruthenium complex $RuH_2(H_2)_2(PCy_3)_2$ (**1**) with 1 equiv of the dicationic heterocyclic carbene precursor $(C_6H_{13}N_3)(SO_3CF_3)_2$ (**3**) produces in good yield the hydrido carbene complex $[RuH(C_6H_{12}N_3)(OSO_2CF_3)(PCy_3)_2][SO_3CF_3]$ (**4**). An X-ray structural analysis of **4** confirms the triflate coordination to the metal. NMR data show that, in solution, **4** exists as a mixture of two isomers. By addition of 1 equiv of the dicationic carbene precursor **3** to the dimer $[Cp^*Ru(\mu\text{-}OMe)]_2$ (**2**), the tricationic bis(carbene) complex $[Cp^*Ru(C_6H_{12}N_3)_2][SO_3CF_3]_3$ (**7**) is isolated in moderate yield and has been characterized by an X-ray structural determination and NMR data.

Introduction

The past few years have seen major developments in the field of carbene chemistry, as illustrated by the publication of several recent reviews.[1] The applications derived from Grubbs' metathesis catalyst $Ru(=CHPh)(Cl)_2(PCy_3)_2$ have a tremendous impact on this area.[2] A breakthrough occurred when N-heterocyclic carbenes were used to favor the formation and stability of electron-deficient intermediates which were proved to be key species in the catalytic cycle: i.e., a monophosphine complex.[3] The synthesis of N-heterocyclic carbenes was reported more than 30 years ago, but a renewed interest developed in the past decade and major contributions came from the groups of Arduengo, Enders, and Herrmann.[4−6] N-Heterocyclic ligands are comparable to phosphines but are stronger σ-donor ligands. In this area, several examples of ruthenium complexes bearing N-heterocyclic carbene ligands have been already reported, with the coordination of the Imes ligand (1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) being probably the most studied.[7] A major improvement was disclosed by Grubbs with the use of a similar mesityl-substituted N-heterocyclic carbene involving a saturated backbone.[8] The latter result highlights the importance of any modification in the structure of the ligand. We have been interested in ruthenium chemistry for many years.[9] We thus decided to investigate the synthesis of ruthenium carbene complexes by using new N-heterocyclic carbenes developed by some of us. The group of Bertrand has recently synthesized dicationic triazolium ligands bearing a proton which can easily be removed in the presence of a base.[10] A cationic carbene is thus produced, the properties of which should differ from those of the neutral diaminocarbenes. We report here the synthesis and characterization of two new ruthenium complexes bearing a triazolidene ligand and preliminary reactivity tests.

Results and Discussion

The two ruthenium complexes $RuH_2(H_2)_2(PCy_3)_2$ (**1**) and $[Cp^*Ru(\mu\text{-}OMe)]_2$ (**2**) were selected as precursors to

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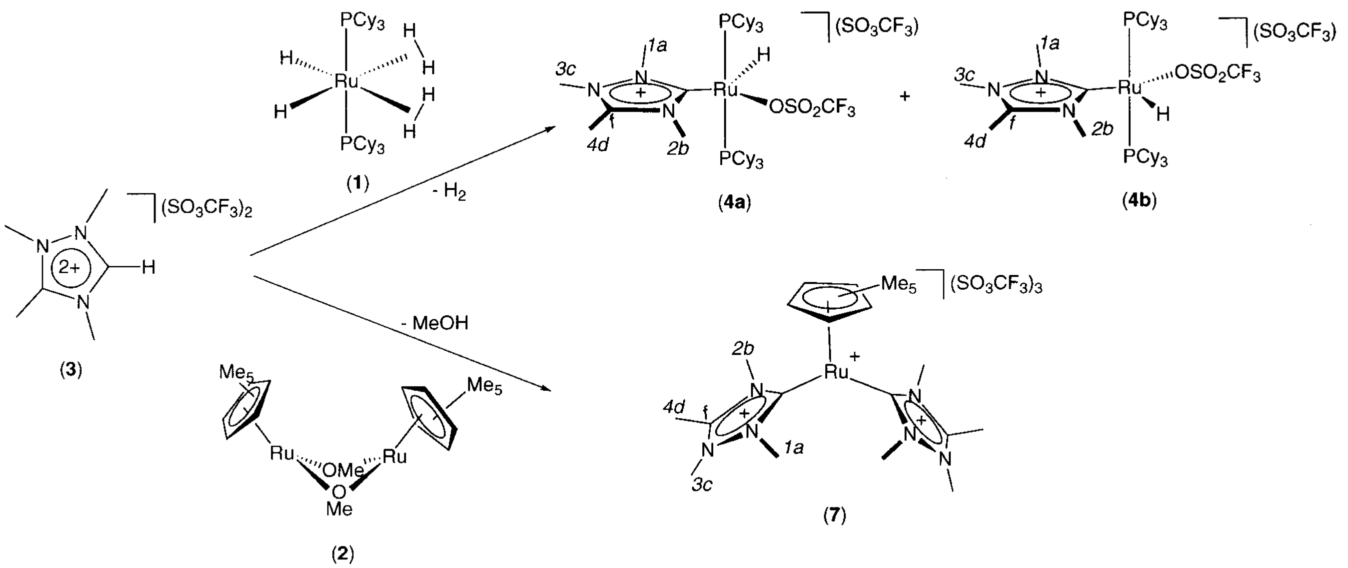
10.1021/om010699x CCC: \$20.00
Publication on Web 11/27/2001

Scheme 1



synthesize new carbene ruthenium complexes. The bis(dihydrogen) complex **1** displays a versatile reactivity characterized by substitution and hydrogen transfer reactions.[9,11] Moreover, the simplest Grubbs carbene complex, $RuCl_2(=CH_2)(PCy_3)_2$, can be obtained by reaction of **1** with dichloromethane.[12] The dimer complex **2** proved to be a good precursor for a wide variety of compounds.[13] In particular, generation of Cp^*Ru^+, a formally 12e fragment, can be achieved by protonation of **2**, and we have previously reported some metathesis activity with this electrophilic fragment.[14] We have chosen to use as a carbene precursor the 1,2,3,4-tetramethyl-1,2,4-triazolium bis(triflate) compound (**3**) (see Scheme 1).[10] The four methyl substituents provide a good NMR probe, and the ligand is stable in air. The properties of this new class of ligands will be described in a future paper.[15]

Synthesis and Characterization of $[RuH(C_6H_{12}N_3)(OSO_2CF_3)(PCy_3)_2][SO_3CF_3]$ (4). By addition of 1 equiv of **3** to a THF solution of **1**, we could isolate an orange solid analyzed as $[RuH(C_6H_{12}N_3)(OSO_2CF_3)(PCy_3)_2][SO_3CF_3]$ (**4**) in 74% yield. Crystals were obtained, allowing an X-ray structural determination (see Figure 1). Crystal data are reported in Table 1. Two phosphines are found in a trans configuration around the ruthenium with a P(1)−Ru−P(2) angle of 164.56(6)°, whereas the carbene ligand and a coordinated triflate are found in an almost perpendicular plane with an angle between the two ligands O(1)−Ru−C(1) of 161.9(3)°. The carbene ligand is characterized by a Ru−C(1) distance of 1.898(6) Å. This value is rather short by comparison to the values reported for ruthenium complexes with the Imes ligand (ca. 2.07 Å) but long compared to those in classical ruthenium carbenes found in Grubbs compounds (typically 1.84 Å).[7a]

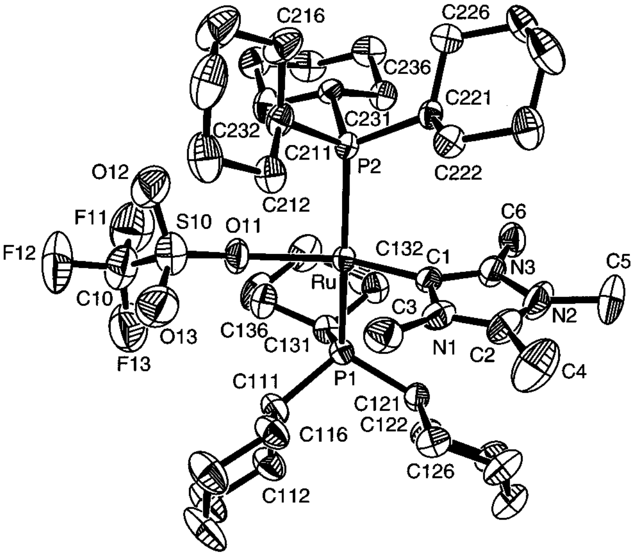


Figure 1. ORTEP drawing of $[RuH(C_6H_{12}N_3)(OSO_2CF_3)(PCy_3)_2][SO_3CF_3]$ (**4**). Selected bond lengths (Å): Ru−C(1), 1.898(6); Ru−P(1), 2.3822(18); Ru−P(2) 2.3953(17); Ru−O(11), 2.235(4); N(1)−N(2), 1.331(9); N(1)−C(1), 1.436(9); N(1)−C(3), 1.417(10); N(2)−C(2), 1.301(10); N(3)−C(1), 1.366(9). Selected bond angles (deg): P(1)−Ru−P(2), 164.54(6); C(1)−Ru−P(1), 93.06(19); C(1)−Ru−P(2), 93.70(19); C(1)−Ru−O(11), 161.9(3); O(11)−Ru−P(1), 85.38(13); O(11)−Ru−P(2), 92.40(13).

^1H, ^{31}P, and ^{13}C NMR data are consistent with the presence in solution of the two isomers **4a**,**b**. ^1H NMR integrations show that these two isomers exist in a constant ratio of 3:1 from room temperature to −70 °C (see Scheme 1). They present very similar spectroscopic data. All the assignments were confirmed by HMQC $^1H-^{13}C$ and NOESY experiments. A single line for the two equivalent phosphines is observed in the $^{31}P\{^1H\}$ NMR spectrum at δ 46.42 for **4a** and δ 45.52 for **4b**. The ^1H NMR spectrum displays two triplets at δ −29.01 and −28.91 with the same J_{P-H} value of 39.5 Hz, which are respectively attributed to the hydride signal of **4a** and **4b**. The very high field resonance is indicative of

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Table 1. Crystallographic Data for Complexes 4 and 7

	4	**7**
chem formula	$[C_{42}H_{78}N_3P_2Ru]$-$[CF_3SO_3]_2$·$^1/_2(CH_3)_2CO$	$[C_{22}H_{39}N_6Ru]$-$[CF_3SO_3]_3$·$3(CH_3)_2CO$
fw	1112.24	1110.11
cryst syst	monoclinic	triclinic
space group	$I2/a$	$P\bar{1}$
Z; calcd density, mg/m^3	8; 1.323	2; 1.514
abs coeff, mm^{-1}	0.478	0.545
$F(000)$	4672	1144
a, Å	26.353(3)	12.0500(18)
b, Å	9.7122(7)	12.5932(17)
c, Å	43.792(5)	16.346(3)
α, deg	90.0	81.513(17)
β, deg	94.792(13)	82.928(19)
γ, deg	90.0	88.205(17)
V, Å	11169.4(19)	2434.5(6)
temp, K	180(2)	160(2)
no. of data/restraints/ params	6777/62/653	4890/301/669
goodness of fit on F^2	1.061	1.039
R1 ($I > 2\sigma(I)$)	0.0714	0.0560
wR2	0.1989	0.1415
largest diff peak and hole, e/Å^3	1.240 and −1.124	1.092 and −0.747

an hydride trans to a vacant site, consistent with a 16e configuration and in agreement with the solid-state structure determined by X-ray diffraction. The carbene ligand for each isomer is characterized by four methyl signals between δ 3.1 and 4.6: the methyl attached to the carbon resonates close to δ 3.1, whereas the three methyls attached to the nitrogen atoms resonate at lower field. By comparison with the starting ligand **3**, the main difference is the disappearance of the signal at δ 10.7 as a result of the deprotonation, the four methyls being little influenced by the coordination. The carbene resonance is observed as a triplet in the $^{13}C\{^1H\}$ NMR spectrum at δ 201.75 for **4a** and δ 203.42 for **4b** with a J_{P-C} value of 11 Hz. By comparison, the carbene resonance in Cp*Ru(IMes)Cl is reported at δ 200.52.[7a] DPFGSE-NOESY experiments show for **4a** a spatial proximity between the hydride and the protons of the methyl CH_3 ^{1} at δ 4.35, whereas for **4b** a spatial proximity between the hydride and the protons of the methyl CH_3 ^{2} at δ 4.11 is observed. These observations allow us to propose the geometries shown in Scheme 1 for **4a**,**b**.

Despite its 16e configuration, **4** is a rather stable complex. No reaction was observed under an atmosphere of dinitrogen or ethylene. However, bubbling air into a CD_3COCD_3 solution of **4** leads to a total conversion into the new complex **5**. ^1H and ^{31}P NMR data allow us to propose for **5** the dioxygen adduct formulation $[RuH(O_2)(C_6H_{12}N_3)(OSO_2CF_3)(PCy_3)_2][SO_3CF_3]$. **5** is obtained as a mixture of the two isomers **5a**,**b** in a 3:1 ratio, as observed for **4a**,**b**. The spectroscopic data are given in the Experimental Section. The most characteristic feature is the rather low field triplet for the hydride at −2.41 ppm (**5a**) and −1.34 ppm (**5b**). We have previously isolated and structurally characterized the cis hydrido dioxygen ortho-metalated complex $RuH(O_2)(P^iPr_3)_2(C_6H_4C_5H_4N)$, which also presents a triplet at −2.65 ppm for the hydride signal.[16] The ^{t}BuNC adduct $[RuH(^tBuNC)(C_6H_{12}N_3)(OSO_2CF_3)(PCy_3)_2][SO_3CF_3]$ (**6**) could also be isolated by addition of 2 equiv of ^{t}BuNC to **4**. The two isomers, in a 3:1 ratio, have been characterized by ^1H and ^{31}P NMR spectroscopy. The shift of the hydride signal to lower field (−8.72 and −8.63 ppm for **6a**,**b**) is in agreement with an 18e configuration. Various silanes were added to **4** in order to favor the triflate decoordination. However, no reaction was obtained with tertiary silanes, whereas decomposition was observed when using secondary or primary silanes.

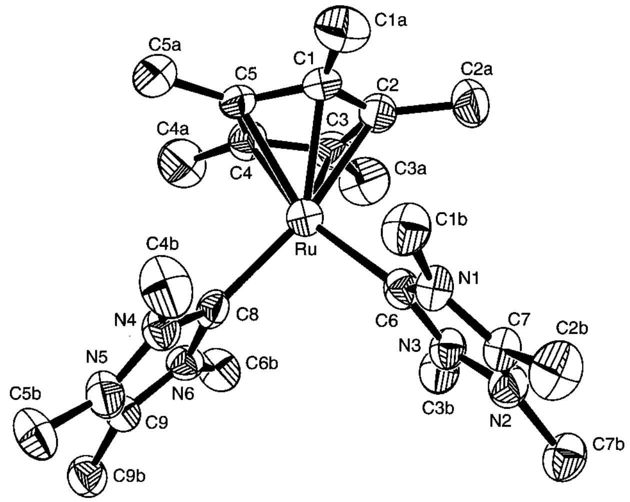

Figure 2. ORTEP drawing of $[Cp^*Ru(C_6H_{12}N_3)_2][SO_3CF_3]_3$ (**7**). Selected bond lengths (Å): Ru−C(1), 2.146(8); Ru−C(2), 2.174(8); Ru−C(3), 2.136(8); Ru−C(4), 2.182(8); Ru−C(5), 2.157(8); Ru−C(6), 2.079(7); Ru−C(8), 2.071(7); N(1)−N(2), 1.363(9); N(1)−C(6), 1.342(9); N(2)−C(7), 1.313(10); N(3)−C(6), 1.346(10); N(3)−C(7), 1.359(9); N(4)−N(5), 1.371(9); N(4)−C(8), 1.349(9); N(5)−C(9), 1.286(9); N(6)−C(8), 1.367(9); N(6)−C(9), 1.351(9). Selected bond angles (deg): C(8)−Ru−C(6), 93.6(3); N(1)−C(6)−N(3), 103.9(6); N(4)−C(8)−N(6), 102.5(6); C(8)−Ru−Cp*, 133.3; C(6)−Ru−Cp*, 133.1.

Synthesis and Characterization of $[Cp^*Ru(C_6H_{12}N_3)_2][SO_3CF_3]_3$ (7). Addition of 1 equiv of the carbene precursor **3** to a THF solution of $[Cp^*Ru(\mu\text{-}OMe)]_2$ (**2**) results in the obtainment upon workup of blue crystals in 37% yield, analyzed as $[Cp^*Ru(C_6H_{12}N_3)_2][SO_3CF_3]_3$ (**7**). The formulation of this tricationic complex was ascertained by NMR (^1H, $^{13}C\{^1H\}$, and HMQC $^1H-^{13}C$) and X-ray data. The molecular structure is shown in Figure 2, and crystal data are reported in Table 1. The coordination around the ruthenium involves the Cp* and two carbene ligands. The rather long Ru−C(6) (2.079(7) Å) and Ru−C(8) (2.071(7) Å) distances are in agreement with two datively bound carbenes acting as 2e donors. These values are in the range of those reported for ruthenium complexes bearing the Imes ligand and slightly longer than in **4**. The C(8)−Ru−C(6) angle is 93.6(3)°, and the two carbenes are symmetrically arranged, as we can see from the angles with the centroid of the Cp* ligand. It is noteworthy that cationic complexes derived from the Cp^*Ru^+ fragment generally achieve an 18e configuration, leading to complexes of the general formula $[Cp^*RuL_2L']^+$, whereas **7** can be stabilized in a 16e configuration. A few stable 16e complexes $[Cp^*RuL_2]^+$ have been previously structurally characterized with a C_{2v} geometry, and like **7**, they all display a characteristic

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[16] Guari, Y.; Donnadieu, B.; Sabo-Etienne, S.; Chaudret, B. To be submitted for publication.

blue color.[17] The ^{1}H NMR spectrum of **7** presents a Cp* signal at δ 1.75 and four signals for the methyl groups of the two equivalent carbene ligands in the range 2.8–4.3 ppm. A high-field shift is thus observed by comparison with the starting ligand **3** or the hydride complex **4**, in agreement with the tricationic formulation. Similarly to **4**, the two carbenic carbons resonate near δ 200.

7 was found to be very stable. No reaction was observed in the presence of ethylene, and no catalytic activity could be detected when testing norbornene ROMP. We have previously reported the reactivity toward neohexene of the Cp*Ru$^+$ fragment, generated from the protonation of **2** by triflic acid. In that case, we observed a complex reaction leading to three classes of products resulting from oligomerization, isomerization, and cracking (methane, C_{11}, and C_{17} hydrocarbons were produced).[14] In the case of **7**, using the same conditions (see Experimental Section), no activity was detected.

The carbonyl complex $[Cp^*Ru(CO)(C_6H_{12}N_3)_2][SO_3CF_3]_3$ (**8**) could be isolated by bubbling CO into an acetone solution of **7**. The carbonyl ligand is characterized by an IR band at 1950 cm^{-1} and a signal at 207.5 ppm in the ^{13}C{^{1}H} NMR spectrum. It is surprising that such a low ν_{CO} stretch is observed for a tricationic species, thus highlighting the unique σ-donating properties of this cationic carbene.

Conclusion

We have described in this paper two new ruthenium complexes bearing a cationic heterocyclic carbene ligand. The carbene precursor was deprotonated directly by the starting ruthenium complex. The bis(dihydrogen) complex **1** easily promotes the deprotonation which is driven by dihydrogen evolution. The hydrido complex **4**, coordinating one carbene ligand, can thus be isolated in good yield. When **1** was reacted with carboxylic acids, protonation in the equatorial plane was also observed, leading to the formation of the hydrido dihydrogen carboxylate complexes $RuH(H_2)(O_2CR)(PCy_3)_2$.[18] These compounds proved to be reactive, and in particular, new complexes were obtained in which a triflate ligand could act either as a counteranion or as a coordinating ligand which may be easily displaced. This suggests that coordination of the triflate ligand is not the factor responsible for the low reactivity of **4**. However, new routes to avoid this coordination will be investigated. In the second case, the deprotonation of the starting ligand **3** by the dimer **2** is more difficult, and the tricationic complex **7** bearing two cationic carbene ligands is obtained only in moderate yield. In the two complexes, the carbene acts as a 2e-donor ligand. Preliminary reactivity tests are rather disappointing and seem to be related to the cationic charge brought by the carbene ligand. Further experiments are underway to evaluate the properties of other transition-metal complexes bearing triazolidene ligands.[15]

Experimental Section

All reactions and manipulations were carried out under an argon atmosphere using standard Schlenk techniques. Solvents were dried and distilled according to standard procedures and degassed prior to use. GC spectra were recorded on an HP 5890 spectrometer. NMR spectra were acquired on Bruker DPX 400 and 300 spectrometers. Microanalysis were performed by the Laboratoire de Chimie de Coordination Microanalytical Service. $Ru(H)_2(H_2)_2(PCy_3)_2$ was synthesized from Ru(COD)(COT) according to published procedures.[11a] The dicationic heterocyclic precursor **3** was obtained following the procedure established by Buron et al.[10] $[Cp^*Ru(\mu\text{-}OMe)]_2$ was generated in situ and directly used in solution according to the published procedures.[13]

Synthesis of $[HRu(PCy_3)_2(OSO_2CF_3)(C_6H_{12}N_3)][OSO_2CF_3]$ (4). $Ru(H)_2(H_2)_2(PCy_3)_2$ (0.100 g, 0.149 mmol) was suspended in 8 mL of THF. Compound **3** (0.064 g, 0.149 mmol) was then added in one portion to the suspension at room temperature. The initial gray solution became slowly yellow until complete dissolution of the suspension. After several minutes, an orange-yellow solid was obtained. After filtration, the solid was dried under a flux of argon and finally under vacuum. Orange crystals were obtained with a mixture of acetone and pentane at room temperature. Yield: 74%. Anal. Calcd for $C_{44}H_{79}F_6N_3O_6P_2S_2Ru$: C, 48.6; H, 7.3; N, 3.8. Found: C, 48.8; H, 7.4; N, 3.6. ^{1}H NMR ($(CD_3)_2CO$, 294 K, 400.13 MHz): **4a**, δ −29.01 (t, 1H, RuH, J_{P-H} = 39.5 Hz), 1−2 (m, PCy$_3$), 3.09 (s, 3H, $CH_3{}^4$), 4.35 (s, 3H, $CH_3{}^1$), 4.38 (s, 3H, $CH_3{}^2$), 4.40 (s, 3H, $CH_3{}^3$); **4b**, δ −28.91 (t,1H, RuH, J_{P-H} = 39.5 Hz), 1−2 (m, PCy$_3$), 3.13 (s, 3H, $CH_3{}^4$), 4.11 (s, 3H, $CH_3{}^2$), 4.43 (s, 3H, $CH_3{}^3$), 4.54 (s, 3H, $CH_3{}^1$). ^{13}C{^{1}H} NMR ($(CD_3)_2CO$, 243 K, 100.61 MHz): **4a**, 9.72 (s, C^dH_3), 35.61 (s, C^aH_3), 36.24 (s, C^cH_3), 37.09 (s, C^bH_3), 121.66 (q, CF$_3$, J_{C-F} = 321 Hz), 151.72 (s, NNC^f), 201.75 (s, RuC^e); **4b**, δ 11.12 (s, C^dH_3), 35.42 (s, C^cH_3), 35.89 (s, C^bH_3), 38.05 (s, C^aH_3), 121.66 (q, CF$_3$, J_{C-F} = 321 Hz), 152.69 (s, NNC^f), 203.42 (s, RuC^e). ^{31}P{^{1}H} NMR ($(CD_3)_2CO$, 294 K, 161.98 MHz): **4a**, δ 46.42; **4b**, δ 45.52.

Reactivity of 4 with Air. Air was introduced via a syringe to an NMR tube containing an acetone-$^2H_6$ solution (0.5 mL) of **4** (10 mg). The initial orange solution progressively turned to a dark orange solution. The contents of the tube were analyzed by NMR spectroscopy. ^{1}H NMR ($(CD_3)_2CO$, 297 K, 250.14 MHz): **5a**, δ −2.41 (t,1H, RuH, J_{P-H} = 26.8 Hz), 1−2.8 (m, PCy$_3$), 3.18 (s, 3H, CH$_3$), 4.68 (s, 3H, CH$_3$), 4.81 (s, 3H, CH$_3$), 5.04 (s, 3H, CH$_3$); **5b**, δ −1.34 (t,1H, RuH, J_{P-H} = 27.7 Hz), 1−2.8 (m, PCy$_3$), 3.18 (s, 3H, CH$_3$), 4.43 (s, 3H, CH$_3$), 4.51 (s, 3H, CH$_3$), 4.54 (s, 3H, CH$_3$). ^{31}P{^{1}H} NMR ($(CD_3)_2CO$, 297 K, 121.26 MHz): **5a**, δ 54.63 (s); **5b**, δ 51.33 (s).

Synthesis of $[HRu(PCy_3)_2(OSO_2CF_3)(C_6H_{12}N_3)(^tBuNC)][OSO_2CF_3]$ (6). ^{t}BuNC (19 μL, 0.16 mmol) was added to an acetone (5 mL) solution of **4** (0.090 g, 0.080 mmol) at room temperature. The orange solution turned immediately to a pale blue-gray color. After 15 min of stirring, the solution was evaporated to dryness, giving an oil. This oil was washed twice with Et$_2$O (3 mL), allowing the formation of a off-white powder. Yield: 86%. Anal. Calcd for $C_{45}H_{88}F_6N_4O_6P_2S_2Ru\cdot 0.5{}^tBuNC$: C, 49.0; H, 8.0; N, 5.4. Found: C, 49.2; H, 7.7; N, 5.6. ^{1}H NMR ($(CD_3)_2CO$, 300 K, 300.13 MHz): **6a,** δ −8.72 (t,1H, RuH, J_{P-H} = 22.5 Hz), 1−2.2 (m, PCy$_3$), 1.64 (s, 9H, ^{t}Bu), 3.21 (s, 3H, CH$_3$), 4.52 (s, 3H, CH$_3$), 4.57 (s, 3H, CH$_3$), 5.01 (s, 3H, CH$_3$); **6b**, δ −8.63 (t,1H, RuH, J_{P-H} = 21 Hz), 1−2.2 (m, PCy$_3$), 1.61 (s, 9H, ^{t}Bu), 3.17 (s, 3H, CH$_3$), 4.52 (s, 3H, CH$_3$), 4.73 (s, 3H, CH$_3$), 4.87 (s, 3H, CH$_3$); free ^{t}BuNC was detected and integrated, δ 1.60 (s, $[^tBuNC]_{0.5}$). ^{31}P{^{1}H} NMR ($(CD_3)_2CO$, 300 K, 121.49 MHz): **6a**, δ 48.41 (s); **6b**, δ 48.41 (s).

Synthesis of $[Cp^*Ru(C_6H_{12}N_3)_2][OSO_2CF_3]_3$ (7). A solution of $[Cp^*RuCl_2]_2$ (0.100 g, 0.162 mmol) and K_2CO_3 (0.25 g, 1.8 mmol) in 8 mL of methanol was stirred and heated during 30 min at 60 °C. The initially brown solution became slowly red. After filtration and evaporation of the solvent under vacuum, $[Cp^*Ru(\mu\text{-}OMe)]_2$ was extracted with 10 mL of THF. The yield was estimated at 90%. Then, 1 equiv of compound **3** (0.0628 g, 0.147 mmol) was added in one portion at room temperature. The solution became brown, and a blue precipi-

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tate was formed. After filtration, the solid was dried under a flux of argon and finally under vacuum. Blue crystals were obtained with a mixture of acetone and pentane at low temperature. Yield: 37%. The yield was not improved when using 2 equiv of **3**. Anal. Calcd for $C_{25}H_{39}F_9N_6O_9S_3Ru$: C, 32.1; H, 4.2; N, 9.0. Found: C, 32.0; H, 3.3; N, 8.3. ^1H NMR ($(CD_3)_2CO$, 294 K, 300.13 MHz): δ 1.75 (s,15H, Cp*), 3.32 (s, 6H, CH_3 ^{4}), 3.89 (s, 6H, CH_3 ^{1}), 4.21 (s, 6H, CH_3 ^{2}), 4.25 (s, 6H, CH_3 ^{3}), $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$, 294 K, 75.47 MHz): δ 10.59 (s, $C_5(CH_3)_5$), 10.54 (s, C^dH_3), 35.39 (s, C^bH_3), 37.71 (s, C^aH_3), 38.63 (s, C^cH_3), 81.4 (s, $C_5(CH_3)_5$), 121.35 (q, CF_3, $J_{C-F} = 321$ Hz), 157.7 (s, NNC^f), 199.5 (s, RuC^e).

Synthesis of $[Cp^*Ru(C_6H_{12}N_3)_2(CO)][OSO_2CF_3]_3$ (8). An acetone (3 mL) solution of **7** (0.046 g, 0.049 mmol) was treated with a slow stream of CO for ca. 5 min, during which time the solution turned pale orange. Addition of 2 mL of pentane allowed the isolation of a beige solid after workup. Yield: 65%. Anal. Calcd for $C_{26}H_{39}F_9N_6O_{10}S_3Ru\cdot0.5(CH_3)_2CO$: C, 33.3; H, 4.3; N, 8.5. Found: C, 33.0; H, 4.3; N, 8.4. ^1H NMR ($(CD_3)_2CO$, 300 K, 300.13 MHz): δ 2.03 (s,15H, Cp*), 2.98 (s, 6H, CH_3), 4.00 (s, 6H, CH_3), 4.36 (s, 6H, CH_3), 4.41 (s, 6H, CH_3); free acetone was detected and integrated, δ 2.10 (s, $[(CH_3)_2CO]_{0.5}$). $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$, 294 K, 75.47 MHz): δ 10.28 (s, $C_5(CH_3)_5$), 11.75 (s, C^dH_3), 36.76 (s, C^bH_3), 38.30 (s, C^aH_3), 38.02 (s, C^cH_3), 100.0 (s, $C_5(CH_3)_5$), 121.43 (q, CF_3, $J_{C-F} = 321$ Hz), 155.6 (s, NNC^f), 188.6 (s, RuC^e), 207.5 (s, CO).

Reaction of 7 with Norbornene. To a solution of norbornene (0.118 g, 1.25 mmol) in 1.4 mL of CH_2Cl_2 was added a solution of **7** (0.0180 g, 1.25 10^{-2} mmol) in 0.6 mL of CH_2Cl_2 at room temperature. No color change of the blue initial solution was observed. The reaction was performed in a Fischer–Porter bottle, and the mixture was stirred overnight. The next day, a blue compound was isolated as the starting complex and the solution analyzed by GC showed unreactive norbornene.

Reaction of 7 with 3,3-Dimethylbut-1-ene. To a solution of **7** (0.0160 g, 1.70 10^{-2} mmol) in 1.4 mL of CD_2Cl_2 was added 21.7 μL of 3,3-dimethylbut-1-ene (0.0140 g, 1.70×10^{-2} mmol). The solution was stirred and heated at 100 °C over 24 h and then analyzed by ^1H NMR spectroscopy.

Crystal Data. Data were collected at low temperature on a Stoe Imaging Plate Diffraction System (IPDS), equipped with an Oxford Cryosystems Cryostream Cooler Device and using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). The final unit cell parameters were obtained by least-squares refinement of a set of 5000 reflections, and crystal decay was monitored by measuring 200 reflections by image. No significant fluctuation of the intensities was observed over the course of the data collection. The structures have been solved by direct methods using SIR92[19] and refined by least-squares procedures on F^2 with the aid of SHELXL.[20] The atomic scattering factors were taken from ref 21. Hydrogen atoms were located on a difference Fourier map and refined by using a riding model. All non-hydrogen atoms were anisotropically refined, a weighting scheme was used in the last cycles of refinement, and a semiempirical absorption correction was applied for the two structures.[22] In the case of **4**, a triflate anion and a half-molecule of acetone were located and found disordered on two sites. The disordered model was refined using some restraints to achieve a chemically reasonable geometry. In the case of **7**, one triflate anion was found statistically distributed on two alternative positions. Restraints were also used to stabilize the model. Moreover, the asymmetrical unit contains three molecules of acetone. In both cases, the disordered models were not completely satisfactory, but any attempts to improve these models failed. This might be responsible for the large discrepancy observed for R1 and wR2. Drawings of the molecules were performed with the program ORTEP32 with 50% probability displacement ellipsoids for non-hydrogen atoms.[23]

Acknowledgment. This work is supported by the CNRS and RHODIA (St Fons, France).

Supporting Information Available: Tables giving X-ray structural information on **4** and **7** and X-ray crystallographic data, as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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