Synthesis, Characterization and Reactivity of New (μ-Aminocarbyne)diruthenium Complexes Containing Alkynylimino Ligands

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Addition of acetylides R′C≡CLi [R′ = Tol, Ph, Me_3Si, *n*Bu, C(Me)=CH_2] to the diruthenium complexes [Ru_2{μ-CN(Me)(R)}(μ-CO)(CO)($NCCMe_3$)$(Cp)_2$]$^+$ (R = Xy, **2a**; Bz, **2b**; Me, **2c**) results in the formation of [Ru_2{μ-CN(Me)(R)}(μ-CO)(CO){N(H)=C(CMe_3)(C≡CR′)}$(Cp)_2$]$^+$ (R = Xy, R′ = Tol, **3a**; R = Bz, R′ = Tol, **3b**; R = Me, R′ = Tol, **3c**; R = Xy, R′ = Ph, **4a**; R = Bz, R′ = Ph, **4b**; R = Me, R′ = Ph, **4c**; R = Bz R′ = H, **5**; R = Xy, R′ = *n*Bu, **6**; R = Xy, R′ = [C(Me)=CH_2], **7**), which contain an alkynylimino ligand, formed from addition of the acetylide to the Me_3CCN ligand. Structural and spectroscopic studies show that all these complexes contain the two Cp ligands in a relative *cis* arrangement, whereas two isomers arise from the different orientation of the substituents on the bridging aminocarbyne μ-CN(Me)(R) when R ≠ Me. Addition of secondary amines to **3**–**7** results in a stereo- and regioselective *cis* amination of the C–C triple bond to give the new complexes [Ru_2{μ-CN(Me)(R)}(μ-CO)(CO){N(H)=C(CMe_3)C(H)=C(NMe_2)(Tol)}$(Cp)_2$]$^+$ (R = Xy, **8a**; Bz, **8b**; Me, **8c**), [Ru_2{μ-CN(Me)(Xy)}(μ-CO)(CO){N(H)=C(CMe_3)C(H)=C(NC_5H_{10})(Tol)}$(Cp)_2$]$^+$(**9**) and [Ru_2{μ-CN(Me)(Xy)}(μ-CO)(CO){N(H)=C(CMe_3)C(H)=C(NMe_2)C(Me)=CH_2)}$(Cp)_2$]$^+$ (**10**) containing the hitherto unknown new imino-2-en-3-amine ligand. The solid-state structures of these products have been analyzed by X-ray analysis and, in solution, by NOE spectroscopic studies.

Introduction

Transition metal complexes containing η^1-coordinated imines represent an important field in classical coordination chemistry and organometallic chemistry.[1−3] Several synthetic routes for their synthesis have been developed in the last decade, including displacement of a labile ligand by free imine and modification of coordinated ligands.[4] Among the latter, some interesting examples are: a) oxidation of coordinated amines;[5] b) condensation of coordinated amines with free aldehydes and ketones;[6] c) reduction of coordinated nitriles.[7,8] Only in a limited number of cases the imino ligands have been obtained via addition of a carbon nucleophile to coordinated nitriles.[8,9] We have recently reported a particular case of the latter procedure employing acetylides as carbon nucleophiles.[10] Thus, addition of TolC≡CLi (Tol = *p*-MeC_6H_4) to [Fe_2{μ-CN(Me)(Xy)}(μ-CO)(CO)($NCCMe_3$)$(Cp)_2$]$^+$ (Xy = 2,6-$Me_2C_6H_3$), followed by protonation, in THF at low temperature, resulted in the formation of the complex [Fe_2{μ-CN(Me)(Xy)}(μ-CO)(CO){N(H)=C(CMe_3)(C≡CTol)}$(Cp)_2$]$^+$, which contains the new alkynylimino ligand HN=C(CMe_3)(C≡CTol). Unfortunately, the reported reaction occurs only in the case described, and, depending on the experimental conditions, other products can be formed. Thus, we have decided to investigate analogous reactions of diruthenium complexes. As will be shown in this paper, the reaction for the synthesis of alkynylimino complexes of ruthenium is very general: aromatic, aliphatic and functionalized acetylides can be used, as well as different groups on the aminocarbyne. Moreover, the high unsaturation of the alkynylimino ligand offers the possibility to exploit it for further modification, and some studies on nucleophilic additions are reported here.

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Results and Discussion

Synthesis and Characterization of the Nitrile Complexes [Ru_2{μ-CN(Me)(R)}(μ-CO)(CO)($NCCMe_3$)$(Cp)_2$]$^+$ (R = Xy, 2a; Bz, 2b; Me, 2c)

One CO ligand in the diruthenium aminocarbyne complexes [Ru_2{μ-CN(Me)(R)}(μ-CO)$(CO)_2(Cp)_2$]$^+$ [R = Xy, **1a**; CH_2Ph (Bz), **1b**; Me, **1c**] [11] can be easily replaced by Me_3CCN after treatment with Me_3NO in THF and a slight excess of the nitrile compound (Scheme 1). The resulting complexes [Ru_2{μ-CN(Me)(R)}(μ-CO)(CO)($NCCMe_3$)$(Cp)_2$]$^+$ (R = Xy, **2a**; Bz, **2b**; Me, **2c**), obtained in good yields (85−88%), have been spectroscopically characterized. The IR spectra of **2a**−**c** show the presence of a terminal and a bridging CO, whereas the ^{1}H and ^{13}C spectra show

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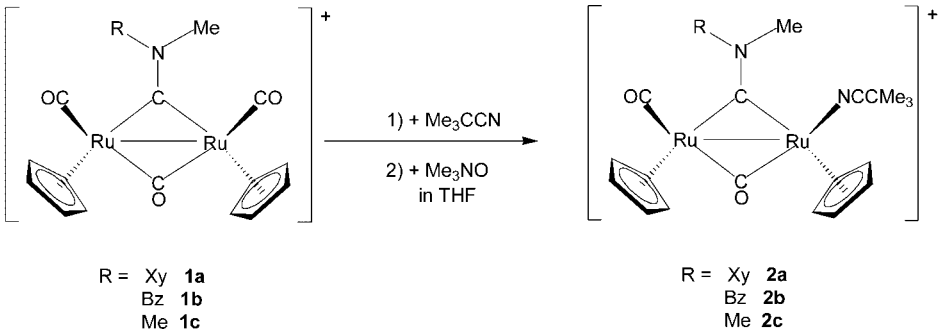


R = Xy **1a**, Bz **1b**, Me **1c**

R = Xy **2a**, Bz **2b**, Me **2c**

Scheme 1

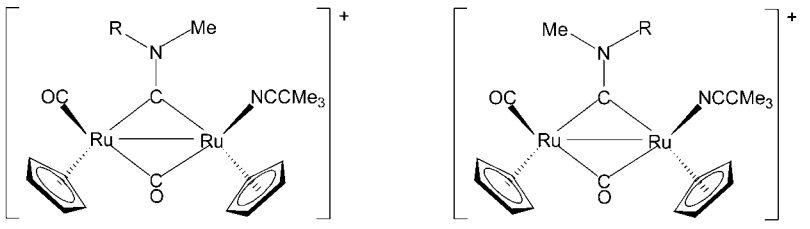
resonances due to two inequivalent Cp ligands. Moreover, resonances typical of the Me_3CCN ligand are present in both the ^1H and ^{13}C NMR spectra, confirming coordination of the nitrile group in complexes **2a**−**c**.

It is worth noting that in the case of **2a,b,** where the bridging aminocarbyne ligand is non-symmetrically substituted, two isomers are present in solution (see Scheme 2, where the two isomers have been labeled α and β; α/β = 1.5), as a consequence of the different orientation of the substituents in the μ-CN(Me)(R) ligand and hindered rotation around the C−N bond.

Another explanation deriving from a possible *cis*−*trans* isomerisation of the two Cp ligands with respect to the Ru_2C_2 plane, is ruled out by the observation of only one isomer in the case of **2c** (R = Me). It is worth noting that the starting compounds **1a**−**c** adopt a *cis*-arrangement,[11] and this is the preferred geometry for the analogous (aminocarbyne)diruthenium and -diiron complexes.[12−14] The fact that the two isomers are due to the orientation of the μ-CN(Me)(R) ligand has been further supported in the case of **2a** by NOE spectroscopic measurements. Some important results arise from these studies: 1) in both isomers, the NOE is mutually generated between the two Cp ligands, as expected for a *cis* geometry. 2) NOE is generated in the major isomer (but not in the minor) between the NMe group and the Me_3CCN ligand. Thus, it is possible to assign the α structure to the major isomer. 3) In perfect agreement with this, NOE is observed in the minor isomer between the protons of the Xy group and the Me_3CCN ligand (β structure). 4) In both the α and β isomers, the Cp resonating at lower frequencies (< 5 ppm) is the one on the same side of the Xy group. It is noteworthy that in **2b,c** both Cp ligands resonate above 5 ppm in the ^1H NMR spectra, suggesting that the shift at lower frequencies of one Cp in **2a** is due to the presence of Xy.

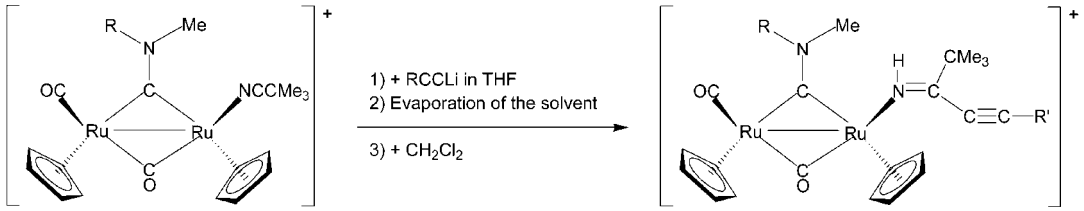
Synthesis and Characterization of the Alkynylimino Complexes $[Ru_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)\{N(H)=C(CMe_3)(C{\equiv}CR')\}(Cp)_2]^+$ (R = Xy, R′ = Tol, 3a; R = Bz, R′ = Tol, 3b; R = Me, R′ = Tol, 3c; R = Xy, R′ = Ph, 4a; R = Bz, R′ = Ph, 4b; R = Me, R′ = Ph, 4c; R = Bz, R′ = H, 5; R = Xy, R′ = *n*Bu, 6; R = Xy, R′ = [C(Me) = CH_2], 7)

The nitrile complexes **2a**−**c** react, in THF at low temperature, with different acetylides R′C≡CLi (R′ = Tol, Ph, Me_3Si, *n*Bu, C(Me)=CH_2) affording, in good yields (56−75%), the new $[Ru_2(\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)\{N(H)=C(CMe_3)(C{\equiv}CR')\}(Cp)_2]^+$ (R = Xy, R′ = Tol, **3a**; R = Bz, R′ = Tol, **3b**; R = Me, R′ = Tol, **3c**; R = Xy, R′ = Ph, **4a**; R = Bz, R′ = Ph, **4b**; R = Me, R′ = Ph, **4c**; R = Bz R′ = H, **5**; R = Xy, R′ = *n*Bu, **6**; R = Xy, R′ = [C(Me)=CH_2], **7**) which contain an alkynylimino ligand, formed from addition of the acetylide to the Me_3CCN ligand (Scheme 3). The hydrogen of the NH group probably arises from the CH_2Cl_2 used to solubilize the residue obtained after evaporation of the THF during the work-up of the reaction (see next section). Interestingly, when $Me_3SiC{\equiv}CLi$ is used, cleavage of the Si−C(sp) bond occurs and, thus, the final product contains a proton instead of $SiMe_3$. Unexpectedly, this is the only way to obtain **5**, since addition of HC≡CNa to **2b** results in decomposition products.



Isomer α Isomer β

Scheme 2



R = Xy **2a**
Bz **2b**
Me **2c**

R=	Xy	Bz	Me	Xy	Bz	Me	Bz	Xy	Xy
R'=	Tol	Tol	Tol	Ph	Ph	Ph	H	Bu	C(Me)=CH$_2$
	3a	**3b**	**3c**	**4a**	**4b**	**4c**	**5**	**6**	**7**

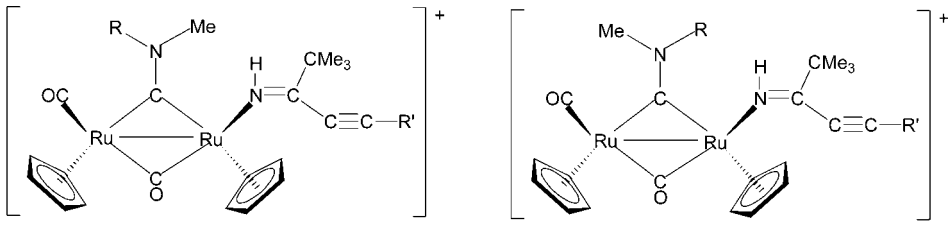
Scheme 3

Complexes **3**−**7** have been fully characterized by IR, ^{1}H and ^{13}C NMR spectroscopy; **3a** has also been characterized by X-ray crystallography, and **3b, 4b** and **5** by ESI MS. The mass spectra confirm the ionic nature of these complexes: a positive ion corresponding to the cation and a negative ion at *m*/*z* = 149, corresponding to $CF_3SO_3^-$ are, in fact, present. The IR spectra of **3**−**7** in CH_2Cl_2 show ν(CO) at ca. 1968 and 1810 cm^{-1} and bands at ca. 2200 cm^{-1} attributable to ν(C≡C); a broad signal at ca. 3320 cm^{-1} (in KBr) is a clear indication of the presence of the NH group. It is worth noting that in the ^{1}H NMR spectra of **3a, 4a, 6** and **7** (R = Xy), one Cp resonates below and one above δ = 5 ppm, whereas in the remaining alkynylimino compounds (R = Bz or Me) both resonances are above δ = 5 ppm, confirming the peculiar shielding effect of the Xy group on the closer Cp ligand. The ^{13}C NMR spectra show four high frequency resonances at δ ca. 310, 236, 202 and 184 ppm, in the typical regions for bridging aminocarbyne, bridging and terminal CO and imine carbon atoms, respectively.

As in **2c**, the NMR spectra of **3c** and **4c** show the presence in solution of only one species, whereas two isomers exist for all the complexes with R ≠ Me (see Scheme 4). The ratio of these isomeric forms is ca. 2:1 for complexes **3b**, **4b** and **5** (R = Bz), and increases up to 10−20:1 for **3a**, **4a**, **6** and **7** (R = Xy), in agreement with the different steric properties of the aminocarbyne substituents: thus, one isomer strongly predominates when the bulkier Xy group is present. Moreover, in all these cases, it can be assumed that the major species is the α-isomer, in which the bulky alkynylimino ligand is on the same side of the less bulky Me group.

The possible presence of *cis*-*trans* forms of the $Cp_2Ru_2(\mu\text{-}C)_2$ core, or of isomers deriving from the C=N iminic double bond, cannot be excluded, but they are less convincing since they would also entail the presence of isomers in the case of complexes with symmetrically substituted aminocarbyne. NOE measurements further support our hypothesis. For example, irradiation of the Cp resonance (δ = 5.46 ppm) of the major isomer of **3a** resulted in the enhancement of the resonances due to the other Cp ligand, the NMe group and some protons of the HN=C(CMe$_3$)(C≡CTol) ligand, in agreement with the proposed *cis*-α structure. Conversely, irradiation of the Cp resonating at lower frequency (δ = 4.95 ppm) affected only the resonance due to the other Cp (δ = 5.46 ppm) and the Xy group. Moreover, in the case of **3b**, because of the higher concentration of the minor isomer than in the case of **3a**, it has been possible to determine the relative orientation of the substituents in both the isomers via NOE measurements. The major isomer shows results similar to the ones reported for the major isomer of **3a**, indicating its *cis*-α structure. Conversely, in the minor isomer of **3b** it has been possible to detect an appreciable NOE between the two Cp ligands, between one Cp and the NMe group, and between the other Cp, the NBz and the alkynylimino ligand confirming a *cis*-β structure.

Further support is given to our stereochemical assignments from the X-ray structure of **3a**, which is reported in Figure 1, whereas relevant bond lengths and angles are reported in Table 1.



Isomer α Isomer β

Scheme 4

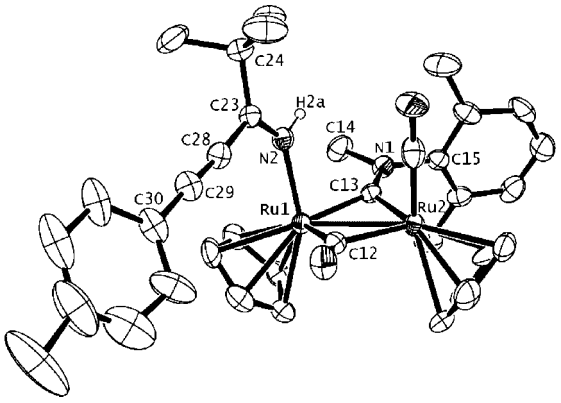


Figure 1. Molecular structure of **3a**, with key atoms labeled (all H atoms, apart from H2a have been omitted). Displacement ellipsoids are at 30% probability level

Table 1. Selected bond lengths (Å) and angles (°) for complex **3a**

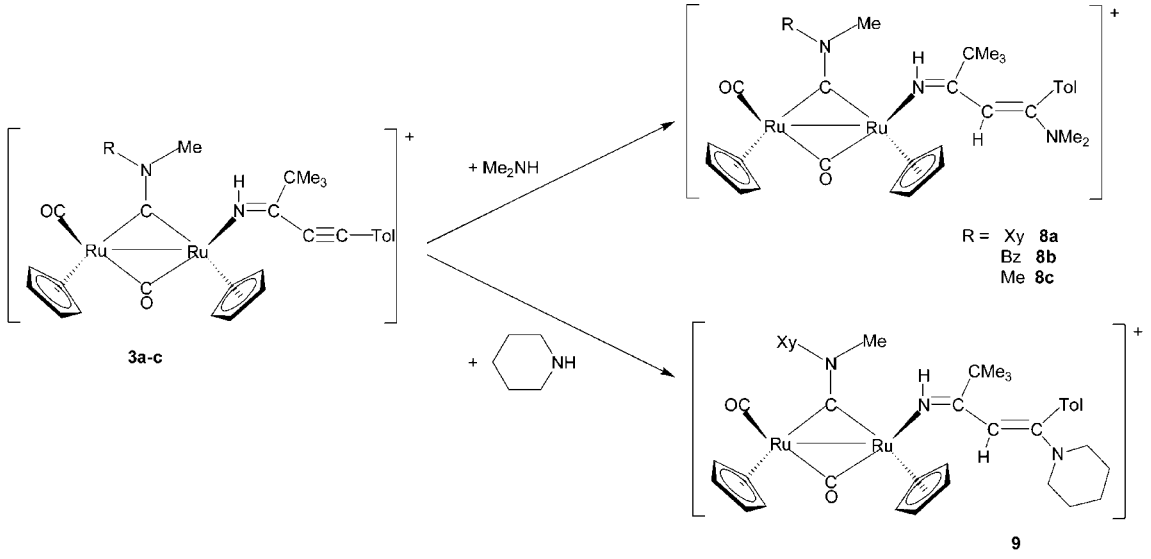
Ru(1)−Ru(2)	2.7105(9)	C(23)−C(24)	1.518(11)
Ru(1)−C(12)	1.985(9)	C(23)−C(28)	1.438(11)
Ru(2)−C(12)	2.113(8)	C(28)−C(29)	1.218(13)
Ru(1)−C(13)	1.963(8)	C(29)−C(30)	1.405(14)
Ru(2)−C(13)	1.973(8)	C(13)−N(1)	1.328(11)
Ru(1)−N(2)	2.090(7)	N(1)−C(14)	1.502(12)
N(2)−C(23)	1.268(11)	N(1)−C(15)	1.432(11)
C(13)−N(1)−C(14)	121.1(7)	N(2)−C(23)−C(28)	119.1(8)
C(13)−N(1)−C(15)	121.4(7)	C(24)−C(23)−C(28)	117.0(7)
C(14)−N(1)−C(15)	117.2(7)	C(23)−C(28)−C(29)	175.0(10)
N(2)−C(23)−C(24)	123.9(7)	C(28)−C(29)−C(30)	176.9(11)

The molecular structure of **3a** is almost identical to the one previously reported for the analogous diiron complex $[Fe_2\{\mu\text{-}CN(Me)(Xy)\}(\mu\text{-}CO)(CO)\{N(H)=C(CMe_3)(C\equiv CTol)\}(Cp)_2]^+$,[10] and it can be better described as composed of two moieties, i.e. the $[Ru_2\{\mu\text{-}CN(Me)(Xy)\}(\mu\text{-}CO)(CO)(Cp_2)]$ unit and the alkynylimino ligand $HN=C(CMe_3)(C\equiv CTol)$. The Ru−Ru distance [2.7105(9) Å] is typical for a Ru−Ru single bond.[15−17] The C(13)−N(1) distance [1.328(11) Å] gives evidence of partial double bond character in the μ-CN(Me)(Xy) ligand, which could be alternatively described as a bridging iminium. The two Cp ligands lie on the same side of the mean plane determined by the inner Ru_2C_2 core in a mutual *cis*-position. Moreover, the bulky xylyl group on the bridging aminocarbyne ligand lies on the opposite side of the alkynylimino ligand. Thus, **3a** adopts, in the solid-state, a *cis*-α structure, which is also the predominant isomer revealed in solution by the NOE studies.

Reactions of $[Ru_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)\{N(H)=C(CMe_3)(C\equiv CR')\}(Cp)_2]^+$

Complexes **3a**−**c** react at room temperature in THF with an excess of Me_2NH or piperidine ($C_5H_{10}NH$) giving good yields (60−70%) of new products which show, from the ESI MS analyses, that the secondary amine has been added to **3a**−**c** without loss of the imino ligand. The ν(CO) and the disappearance of ν(C≡C) in the IR spectra suggests that addition has occurred on the C≡C bond; hence, the new products can be formulated as $[Ru_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)\{N(H)=C(CMe_3)C(H)=C(NMe_2)(Tol)\}(Cp)_2]^+$ (R = Xy, **8a**; Bz, **8b**; Me, **8c**) and $[Ru_2\{\mu\text{-}CN(Me)(Xy)\}(\mu\text{-}CO)(CO)\{N(H)=C(CMe_3)C(H)=C(NC_5H_{10})(Tol)\}(Cp)_2]^+$ (**9**) (Scheme 5).

Amination of alkynes is a widely used reaction in organic chemistry, and is promoted by a large variety of transition metals.[18] In our case, the reaction can be better viewed as the amination of an α,β-unsaturated imine η^1-coordinated to ruthenium. The reaction seems to be completely stereo- and regioselective. Amination of **3c**, which exists in solution as a single isomer, results in the formation of only a single species, whereas, amination of the complexes **3a,b**, which



Scheme 5

exist as two isomers (α and β) results in the formation of two products in the same ratio of the starting compounds (in the case of **8a** the concentration of the minor isomer is too low to be fully characterized).

In order to understand better the stereo- and regiochemistry of the addition, an X-ray study has been carried out on **8a**. The molecular structure of **8a** is reported in Figure 2, whereas the relevant bond lengths and angles are reported in Table 2. The molecule is chiral, but the racemic mixture is present within the crystal; two independent molecules are present in the asymmetric unit, with similar relative arrangement of the atoms, similar bond lengths and bond angles but opposite absolute structure. Differences are mainly attributable to packing effects and, in all cases, the parameters describing the bonds in the two molecules fall in the same ranges expected for a similar hybridization of the atoms and bond order. As in the case of **3a**, the structure of **8a** can be discussed in terms of two moieties, i.e. the $Ru_2\{\mu\text{-}CN(Me)(Xy)\}(\mu\text{-}CO)(CO)(Cp_2)$ unit and the new $HN{=}C(CMe_3)CH{=}C(NMe_2)(Tol)$ ligand. The former resembles the analogous unit in **3a** and does not need any further comments; it is, however, worth noting the fact that in this case the molecule also adopts a *cis*-α structure considering the relative position of the two Cp ligands and the orientation of the N(Me)(Xy) group on the aminocarbyne.

The new $HN{=}C(CMe_3)CH{=}C(NMe_2)(Tol)$ ligand is an imino-2-en-3-amine η^1-coordinated to one ruthenium atom via the imino nitrogen [Ru(1)−N(2) 2.077(13) and Ru(3)−N(5) 2.133(13) Å]. In agreement with this, the N(2)−C(13) [1.282(13) Å], N(5)−C(63) [1.248(13) Å], C(18)−C(19) [1.34(2) Å] and C(68)−C(69) [1.35(2) Å] distances are typical double bonds (compare 1.28 Å in free imines and oximes and 1.32 Å in ethylene for typical C=N and C=C, respectively),[19] whereas the C(13)−C(18) [1.493(14) Å] and C(63)−C(68) [1.502(15) Å] interactions are essentially single bonds {compare C(13)−C(14) [1.56(2) Å] and C(63)−C(64) [1.55(2) Å]}, suggesting the absence of conjugation between the imine and enamine. In fact, their two π-systems are nearly orthogonal [dihedral angles N(2)−C(13)−C(18)−C(19) −99.0(19)° and N(5)−C(63)−C(68)−C(69) 101(2)°]. The atoms of the enamine in the two molecules are nearly in the same plane [mean deviations 0.0510 and 0.0467 Å from the least-squares planes C(13)−C(18)−C(19)−N(3)−C(22) and C(63)−C(68)−C(69)−N(6)−C(72), respectively], and they all have sp^2 hybridization. These planes form relatively small angles with the planes of the NMe_2 units [i.e. 22.58(0.97) and 27.74(1.03)° for the two molecules], whereas the Tol groups lie considerably out of the enamine planes, with angles of 49.83(0.42) and 50.19(0.46)° for the two molecules, respectively.

On the basis of the X-ray analysis it is possible to conclude that the amination of the coordinated alkynylimine occurs in a *cis* fashion with the nucleophile adding regioselectively to the β-carbon. The nature of compound **8** and **9** has been further confirmed by IR and NMR spectroscopy. The IR spectra of **8** and **9** in CH_2Cl_2 show two ν(CO) at ca. 1965 and 1808 cm^{-1}, due to the terminal and bridging carbonyl, respectively, whereas a band at ca. 3325 cm^{-1} in the spectra in KBr is attributable to the NH stretching. The NMR spectra of **8** and **9** have been fully assigned using DEPT, gs-HSQC and gs-HMBC experiments.[20] The main features of the ^1H spectra are the presence of two inequiva-

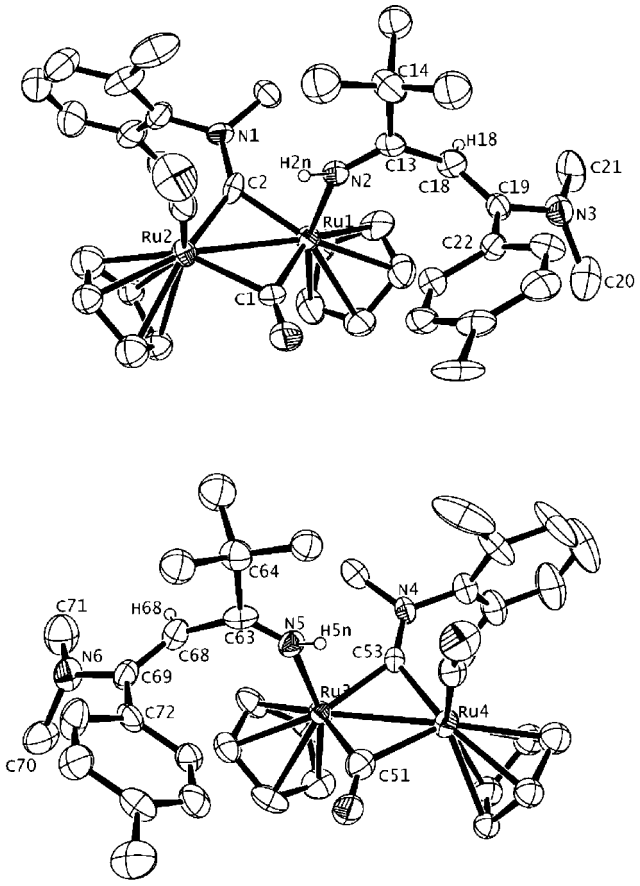
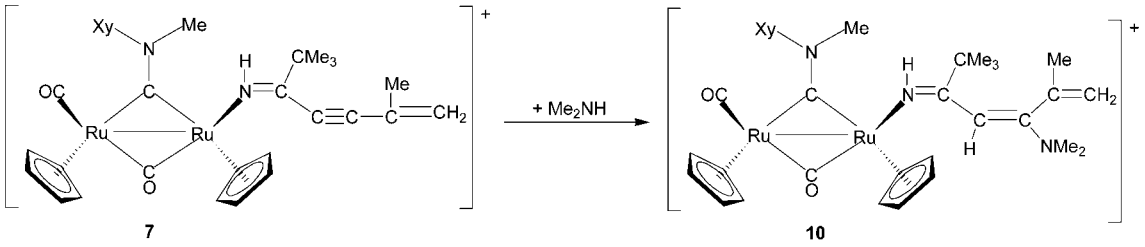


Figure 2. Molecular structure of the two independent molecules of **8a**, with key atoms labeled (all H atoms, apart from H2a, H18, H5n and H68 have been omitted). Displacement ellipsoids are at 30% probability level.

Table 2. Selected bond lengths (Å) and angles (°) for complex **8a**

Ru(1)−Ru(2)	2.7036(16)	Ru(3)−Ru(4)	2.7075(17)
Ru(1)−C(1)	1.965(17)	Ru(3)−C(51)	1.981(17)
Ru(2)−C(1)	2.096(16)	Ru(4)−C(51)	2.071(18)
Ru(1)−C(2)	1.922(13)	Ru(3)−C(53)	1.930(12)
Ru(2)−C(2)	1.967(14)	Ru(4)−C(53)	1.986(12)
Ru(1)−N(2)	2.077(13)	Ru(3)−N(5)	2.133(13)
N(1)−C(2)	1.335(13)	N(4)−C(53)	1.312(13)
N(2)−C(13)	1.282(13)	N(5)−C(63)	1.248(13)
C(13)−C(18)	1.493(14)	C(63)−C(68)	1.502(15)
C(13)−C(14)	1.56(2)	C(63)−C(64)	1.55(2)
C(18)−C(19)	1.34(2)	C(68)−C(69)	1.35(2)
C(19)−N(3)	1.402(18)	C(69)−N(6)	1.393(19)
C(19)−C(22)	1.493(15)	C(69)−C(72)	1.443(17)
N(2)−C(13)−C(18)	118.1(13)	N(5)−C(63)−C(68)	120.2(12)
C(13)−C(18)−C(19)	127.4(13)	C(63)−C(68)−C(69)	128.6(15)
C(18)−C(19)−N(3)	121.6(13)	C(68)−C(69)−N(6)	119.8(14)
C(18)−C(19)−C(22)	122.4(13)	C(68)−C(69)−C(72)	121.1(14)
N(3)−C(19)−C(22)	115.3(12)	N(6)−C(69)−C(72)	119.1(13)



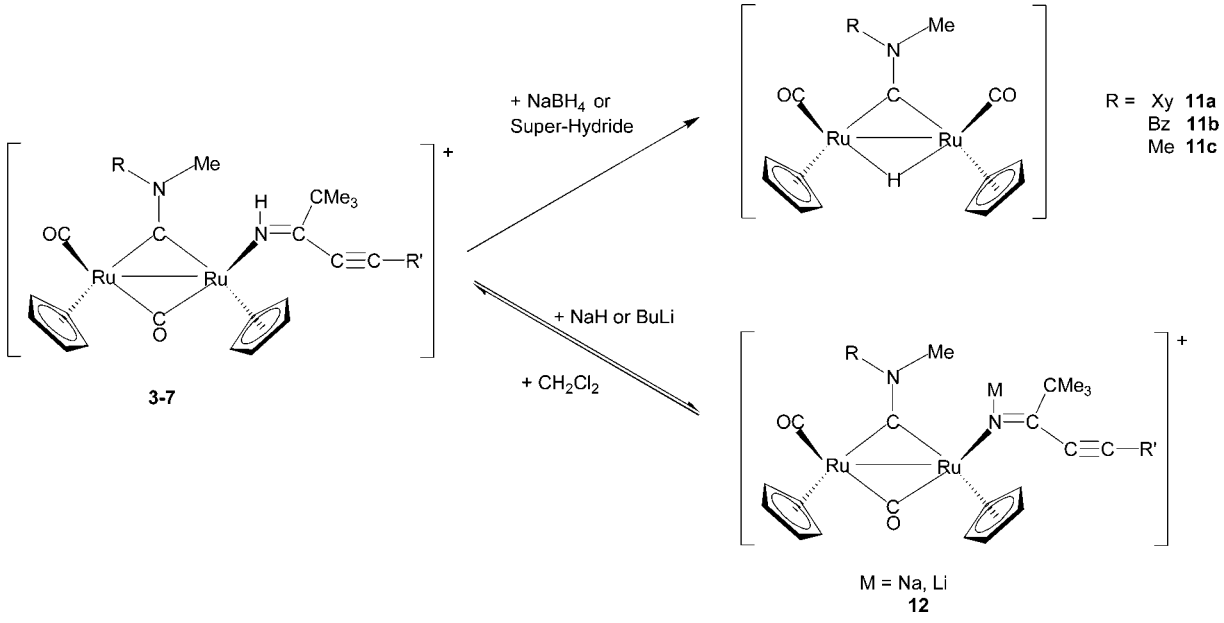
Scheme 6

lent Cp ligands, a broad resonance at δ ca. 6.5 ppm due to the iminic NH and a singlet at δ ca. 5 ppm due to the olefinic α-CH proton. Four different resonances at high frequency are present in the ^{13}C NMR spectra due to the bridging carbyne (ca. 310 ppm), the bridging CO (δ ca. 236 ppm), the terminal CO and the carbon of the imine (both at δ ca. 200 ppm). The α-CH olefinic carbon resonates at ca. 100 ppm, whereas the quaternary β-carbon resonates at δ = 155−156 ppm.

The NMR spectra of **8c** show the presence in solution of a single isomer, whereas two isomers are present in the case of **8a,b** and **9**, with ratios which perfectly correspond to the isomer ratios in the starting compounds **3a,b**. Therefore, it is possible to conclude that, in these cases, the two isomers present in solution are also the α and β isomers arising from the different orientation of the R- and Me groups on the aminocarbyne. The stereochemistry of all the addition products has been further confirmed by NOE experiments. For example, irradiation of the olefinic α-CH proton (δ = 5.20 ppm) of the major isomer of **9** resulted in the enhancement of the resonances due to the α-protons of the piperidine (δ = 3.11 ppm) and the Cp at higher frequency (δ = 5.38 ppm). In the same way, NOE was generated on the olefinic α-CH resonance, on the Cp resonating at δ = 4.98 ppm and in the aminocarbyne NMe resonance by irradiation of the Cp resonance at δ = 5.38 ppm. These data confirm that in this case the amination has occurred with a *cis* geometry and that the imino ligand in the major isomer is on the same side as the Me group of the aminocarbyne ligand (α isomer). Moreover, it is noteworthy that in this case the Cp resonating at lower frequency (δ = 4.98 ppm) is the one on the same side of the Xy group. The NOE observed on one Cp ligand when the other is irradiated agrees with a *cis* arrangement of the $Ru_2\{\mu\text{-}CN(Me)(Xy)\}(\mu\text{-}CO)(CO)(Cp)_2$ core.

Finally, the amination of **7**, which contains an iminoalkynyl ligand conjugated with an olefinic end group, i.e. $HN{=}C(CMe_3)C{\equiv}CC(Me){=}CH_2$, occurs regioselectively onto the C≡C bond affording the complex $[Ru_2\{\mu\text{-}CN(Me)(Xy)\}(\mu\text{-}CO)(CO)\{N(H){=}C(CMe_3)C(H){=}C(NMe_2)C(Me){=}CH_2\}(Cp)_2]^+$ (**10**) which contains the new 1-imino-2,4-dien-3-amine ligand $HN{=}C(CMe_3)CH{=}C(NMe_2)C(Me){=}CH_2$, in a 52% yield. In this case, the reaction is stereoselective, resulting only in the formation of the *cis* addition product (Scheme 6), as shown by NOE experiments.

Strong nucleophiles such as $NaBH_4$ or super-hydride ($LiBHEt_3$) react with **3**−**7** replacing the alkynylimino li-



Scheme 7

gand to give the hydrido complexes $[Ru_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}H)(CO)_2Cp_2]$ (R = Xy, **11a**, Bz, **11b**; Me, **11c**),[21] whereas the reaction with nucleophiles having strong basic character such as NaH and *n*BuLi results in the almost quantitative formation of a new species, tentatively formulated as **12** (Scheme 7). Because of their instability, the latter compounds have not been isolated, but only characterised by IR spectroscopy. Compounds **12** show one terminal and one bridging ν(CO) absorption at wavenumbers similar to those of the cationic derivatives **3**−**7:** 1958 vs and 1803 s for the product obtained from **3a** and *n*BuLi, which should be compared with the IR spectrum of **3a** in THF (1961 vs, 1811 s). The reaction can easily be reversed by evaporation of the solvent in vacuo followed by dissolution of the residue in CH_2Cl_2. A simple explanation could be that metalation of the nitrogen of the imino ligand occurs and, thus, the new products can be formulated as $[Ru_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)\{N(M)=C(CMe_3)(C\equiv CR')\}(Cp_2)]^+$ (M = Li, Na, **12**). An alternative could be deprotonation of the NH instead of metalation, but this would afford a neutral azavinylidene species, in contrast with the IR data. It is noticeable that deprotonation of coordinated imines to give azavinylidene is quite well documented in the literature, whereas metalation is more rare.[4,22,23] Complexes of type **12** are also the product directly formed in THF during the reaction of **2a**−**c** with R′C≡CLi; the alkynylimino products **3**−**7** are, in fact, formed only after evaporation of THF and dissolution of the residue in CH_2Cl_2 (see above).

Conclusion

Nitriles are reported to be labile ligands and, therefore, very often used as intermediates for substitution reactions in organometallic chemistry. Nonetheless, addition of nucleophiles such as amines, alcohols and water have been extensively used for the synthesis of a large variety of metal complexes containing ligands such as azavinylidenes, amides, imidic esters and aminidines.[24,25] Addition of carbon nucleophiles is also known, although less common.[8,26] Despite our recent findings which demonstrated that the addition of acetylides to the nitrile ligand in (aminocarbyne)diiron complexes occurs only in one specific case,[10] we show here that the corresponding reaction is quite general for ruthenium: different substituents on the aminocarbyne have been used (i.e. Xy, Bz, Me) as well as aromatic and aliphatic acetylides. The alkynylimino complexes **3**−**7** are the only products formed in all the cases studied. Therefore, it seems that in the case of ruthenium there is no tendency at all for coupling between the imino and the aminocarbyne ligand, as found in the iron complex. Moreover, in the case of ruthenium it is not necessary to add strong acids, since the acidity of CH_2Cl_2 is sufficient for protonating the nitrogen, whereas the iron analogue requires the addition of strong acids. This suggests an enhanced basicity of the nitrogen in the case of ruthenium compared to iron, which could explain the different output of the two reactions.

The new alkynylimino ligand shows electrophilic properties. Nonetheless, it is not possible to use nucleophiles with a strong basic character, since they metalate the iminic nitrogen rather than adding to the triple bond. Conversely, strong nucleophiles such as $NaBH_4$ gives substitution and not addition. Thus, addition to the alkynylimino ligand can be achieved only using nucleophiles which are not too strong and not too basic, and here the case of secondary amines has been described. The reaction is completely regio- and stereoselective, resulting only in the addition to the β carbon of the ligand and protonation of the α carbon in a *cis* fashion. The resulting ligand can be described as an imino-2-en-3-amine ligand, which, as far as we know, has not been reported before. The procedure elaborated in this paper seems to be an interesting method of synthesizing new bimetallic complexes containing highly unsaturated ligands with heteroatoms.

Experimental Section

All reactions were carried out routinely under nitrogen using standard Schlenk techniques. Solvents were distilled immediately before use under nitrogen from appropriate drying agents. Infrared spectra were recorded with a Perkin−Elmer Spectrum 2000 FT-IR spectrophotometer and elemental analyses were performed on a ThermoQuest Flash 1112 Series EA Instrument. ESI MS spectra were recorded with a Waters Micromass ZQ 4000 with samples dissolved in CH_3CN. All NMR measurements were performed with Varian Gemini 300, Mercury 400 and Inova 600 instruments. The chemical shifts for ^1H and ^{13}C NMR spectra were referenced to internal TMS. The spectra were fully assigned via DEPT experiments and ^1H,^{13}C NMR spectra correlation through gs-HSQC and gs-HMBC experiments.[20] In some cases it has not been possible to assign all the resonances to the minor isomer, especially when it was present in very low concentration. NOE measurements were recorded using the DPFGSE-NOE sequence.[27] All chemicals were used as received from Aldrich Co., except $[Ru_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)_2(Cp)_2][CF_3SO_3]$ (R = Xy, **1a**; Bz, **1b**; Me, **1c**) which were prepared by published methods.[11] The acetylides R′C≡CLi [R′ = Tol, Ph, Me_3Si, *n*Bu, $C(Me)=CH_2$] were prepared just before use from the reaction of the appropriate alkyne R′C≡CH in THF at −50 °C with *n*BuLi (alkyne/*n*BuLi, 1.2).

$[Ru_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)(NCCMe_3)(Cp)_2][CF_3SO_3]$ (R = Xy, 2a; Bz, 2b; Me, 2c). General Procedure: Me_3NO (30.0 mg, 0.400 mmol) was added to a solution containing $[Ru_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)_2(Cp)_2][CF_3SO_3]$ (0.200 mmol) and Me_3CCN (0.1 mL, 0.905 mmol) in THF (5 mL). The resulting suspension was stirred at room temperature for 3 h and, then, the solid removed by filtration through a Celite pad. The solvent was removed under reduced pressure and the residue washed with petroleum ether (2 × 5 mL) and Et_2O (2 × 5 mL) affording the final product as a yellow-orange powder.

2a: $C_{28}H_{31}F_3N_2O_5Ru_2S$ (766.77): calcd. C 43.86, H 4.08, N 3.65; found C 44.02, H 3.99, N 3.54. Yield: 135.0 mg, 88%. ^1H NMR (300.04 MHz, $CDCl_3$, 25 °C) α-Isomer: δ = 1.26 (s, 9 H, CMe_3), 2.23, 2.42 (s, 6 H, $Me_2C_6H_3$), 4.30 (s, 3 H, N*Me*), 4.98, 5.38 (s, 10 H, *Cp*), 7.10−7.36 (m, 3 H, $Me_2C_6H_3$) ppm; β-Isomer: δ = 1.22 (s, 9 H, CMe_3), 2.19, 2.42 (s, 6 H, $Me_2C_6H_3$), 4.22 (s, 3 H, N*Me*), 4.71, 5.58 (s, 10 H, *Cp*), 7.10−7.36 (m, 3 H, $Me_2C_6H_3$) ppm. α/β =

1.5. ^{13}C NMR (75.457 MHz, $CDCl_3$, 25 °C) α-Isomer: δ = 17.2, 18.2 (*Me*$_2$C$_6$H$_3$), 27.3 (C*Me*$_3$), 30.3 (*C*Me$_3$), 53.0 (N*Me*), 88.1, 89.7 (*Cp*), 128.6, 128.7, 129.4 (*C*H Me$_2$C$_6$H$_3$), 128.8, 131.7 (*C*Me Me$_2$C$_6$H$_3$), 134.3 (Me$_3$C*C*N), 147.6 (*C-ipso* Me$_2$C$_6$H$_3$), 200.4 (*C*O), 236.5 (μ-*C*O), 310.6 (μ-*C*) ppm; β-Isomer: δ = 17.6, 18.3 (*Me*$_2$C$_6$H$_3$), 27.4 (C*Me*$_3$), 30.4 (*C*Me$_3$), 54.6 (N*Me*), 87.2, 90.6 (*Cp*), 128.6, 128.7, 129.4 (*C*H Me$_2$C$_6$H$_3$), 128.8, 131.7 (*C*Me Me$_2$C$_6$H$_3$), 133.9 (Me$_3$C*C*N), 147.5 (*C-ipso* Me$_2$C$_6$H$_3$), 200.0 (*C*O), 235.2 (μ-*C*O), 310.2 (μ-*C*) ppm. IR (CH_2Cl_2, 25 °C): $\tilde{\nu}$ = 1982 vs (CO), 1819 s (μ-CO), 1529 m (C=N) cm^{-1}.

2b: $C_{27}H_{29}F_3N_2O_5Ru_2S$ (752.74): calcd. C 43.08, H 3.88, N 3.72; found C 42.92, H 3.97, N 3.52. Yield: 128.0 mg, 85%. ^{1}H NMR (300.04 MHz, $CDCl_3$, 25 °C) α-Isomer: δ = 1.18 (s, 9 H, C*Me*$_3$), 3.90 (s, 3 H, N*Me*), 5.30, 5.48 (s, 10 H, *Cp*), 5.63, 5.64 (d, AB, $^2J_{H,H}$ = 14.3 Hz, 2 H, C*H*$_2$Ph), 7.26−7.48 (m, 3 H, Me$_2$C$_6$*H*$_3$) ppm; β-Isomer: δ = 1.20 (s, 9 H, C*Me*$_3$), 3.82 (s, 3 H, N*Me*), 5.26, 5.51 (s, 10 H, *Cp*), 5.67, 5.78 (d, AB, $^2J_{H,H}$ = 14.8 Hz, 2 H, C*H*$_2$Ph), 7.26−7.48 (m, 3 H, Me$_2$C$_6$*H*$_3$) ppm. α/β = 1.5. ^{13}C NMR (75.457 MHz, $CDCl_3$, 25 °C) α-Isomer: δ = 27.6 (C*Me*$_3$), 30.5 (*C*Me$_3$), 49.1 (N*Me*), 70.6 (*C*H$_2$Ph), 88.0, 90.3 (*Cp*), 127.4−134.2 (Ph + Me$_3$C*C*N), 200.8 (*C*O), 237.0 (μ-*C*O), 304.6 (μ-*C*) ppm; β-Isomer: δ = 27.7 (C*Me*$_3$), 30.6 (*C*Me$_3$), 50.4 (N*Me*), 70.2 (*C*H$_2$Ph), 87.8, 90.5 (*Cp*), 127.4−134.2 (Ph + Me$_3$C*C*N), 200.0 (*C*O), 237.8 (μ-*C*O), 304.3 (μ-*C*) ppm. IR (CH_2Cl_2, 25 °C): $\tilde{\nu}$ = 1980 vs (CO), 1817 s (μ-CO), 1588 w, 1573.7 m, 1550 w (C=N) cm^{-1}.

2c: $C_{21}H_{25}F_3N_2O_5Ru_2S$ (676.64): calcd. C 37.28, H 3.72, N 4.14; found C 37.09, H 3.84, N 4.01. Yield: 117.7 mg, 87%. ^{1}H NMR (300.04 MHz, $CDCl_3$, 25 °C): δ = 1.14 (s, 9 H, C*Me*$_3$), 3.98, 4.06 (s, 6 H, N*Me*$_2$), 5.19, 5.39 (s, 10 H, Cp) ppm. ^{13}C NMR (75.457 MHz, $CDCl_3$, 25 °C): δ = 27.6 (C*Me*$_3$), 30.5 (*C*Me$_3$), 52.2, 53.4 (N*Me*$_2$), 89.9, 90.1 (Cp), 133.5 (Me$_3$C*C*N), 200.0 (*C*O), 237.8 (μ-*C*O), 302.6 (μ-*C*) ppm. IR (CH_2Cl_2, 25 °C): $\tilde{\nu}$ = 1978 vs (CO), 1815 s (μ-CO), 1599 m (C=N) cm^{-1}.

[Ru$_2${μ-CN(Me)(R)}(μ-CO)(CO){N(H)=C(CMe$_3$)(C≡CR′)}(Cp$_2$)]$^+$ (R = Xy, R′ = Tol, 3a; R = Bz, R′ = Tol, 3b; R = Me, R′ = Tol, 3c; R = Xy, R′ = Ph, 4a; R = Bz, R′ = Ph, 4b; R = Me, R′ = Ph, 4c; R = Bz, R′ = H, 5; R = Xy, R′ = *n*Bu, 6; R = Xy, R′ = [C(Me)=CH$_2$], 7). General Procedure: A solution of the appropriate acetylide R′C≡CLi (0.225 mmol) in THF (3 mL) was added dropwise to a solution of **2a−c** (0.150 mmol) in THF (6 mL) at −50 °C and the resulting red solution stirred at room temperature for 30 minutes. Then, the solvent was removed in vacuo and the residue dissolved in CH_2Cl_2 (5 mL) and chromatographed through an Al_2O_3 column. The final product was obtained as an orange fraction using CH_3CN as eluent.

3a: $C_{37}H_{39}F_3N_2O_5Ru_2S$ (882.93): calcd. C 50.33, H 4.45, N 3.17; found C 50.52, H 4.27, N 3.09. Yield: 86.1 mg, 65%. ^{1}H NMR (599.738 MHz, $CDCl_3$, 25 °C) α-Isomer: δ = 1.15 (s, 9 H, C*Me*$_3$), 2.21, 2.44 (s, 6 H, *Me*$_2$C$_6$H$_3$), 2.43 (s, 3 H, *p-Me*C$_6$H$_4$), 4.41 (s, 3 H, N*Me*), 4.95, 5.46 (s, 10 H, *Cp*), 7.10−7.65 (m, 7 H, Me$_2$C$_6$*H*$_3$ + *p*-MeC$_6$*H*$_4$) 7.45 (br., 1 H, N*H*) ppm; β-Isomer: δ = 1.09 (s, 9 H, C*Me*$_3$), 2.11, 2.48 (s, 6 H, *Me*$_2$C$_6$H$_3$), 2.40 (s, 3 H, *p-Me*C$_6$H$_4$), 4.24 (s, 3 H, N*Me*), 4.87, 5.62 (s, 10 H, *Cp*), 7.10−7.65 (m, 8 H, Me$_2$C$_6$*H*$_3$ + *p*-MeC$_6$*H*$_4$ + N*H*) ppm. α/β = 10. ^{13}C NMR (75.457 MHz, $CDCl_3$, 25 °C) α-Isomer: δ = 17.5, 18.4 (*Me*$_2$C$_6$H$_3$), 21.8 (*p-Me*C$_6$H$_4$), 26.8 (C*Me*$_3$), 42.2 (*C*Me$_3$), 53.2 (N*Me*), 89.0, 89.8 (*Cp*), 105.8, 117.0 (*C*≡*C*), 128.1−148.2 (Me$_2$*C*$_6$H$_3$ + *p*-Me*C*$_6$H$_4$), 184.3 (*C*=N), 201.7 (*C*O), 236.0 (μ-*C*O), 311.7 (μ-*C*) ppm; β-Isomer: δ = 17.8, 18.6 (*Me*$_2$C$_6$H$_3$), 21.7 (*p-Me*C$_6$H$_4$), 27.2 (C*Me*$_3$), 41.4 (*C*Me$_3$), 55.4 (N*Me*), 88.1, 91.2 (*Cp*), 105.8, 116.7 (*C*≡*C*), 128.1−148.2 (Me$_2$*C*$_6$H$_3$ + *p*-Me*C*$_6$H$_4$), 183.3 (*C*=N), 202.0 (*C*O), 236.0 (μ-*C*O), 312.7 (μ-*C*) ppm. IR (CH_2Cl_2, 25 °C): $\tilde{\nu}$ = 2200 m (C≡C), 1968 vs (CO), 1811 s (μ-CO), 1560 w, 1508 m (C=N) cm^{-1}. IR (KBr, 25 °C): $\tilde{\nu}$ = 3314 ms (NH) cm^{-1}.

3b: $C_{36}H_{37}F_3N_2O_5Ru_2S$ (868.91): calcd. C 49.76, H 4.29, N 3.22; found C 49.21, H 4.59, N 3.79. Yield: 86.0 mg, 66%. ^{1}H NMR (300.04 MHz, $CDCl_3$, 25 °C) α-Isomer: δ = 1.07 (s, 9 H, C*Me*$_3$), 2.33 (s, 3 H, *p-Me*C$_6$H$_4$), 3.95 (s, 3 H, N*Me*), 5.40, 5.50 (s, 10 H, *Cp*), 5.56, 5.67 (d, AB, $^2J_{H,H}$ = 14.1 Hz, 2 H, C*H*$_2$Ph), 7.04−7.56 (m, 10 H, C$_6$*H*$_5$ + *p*-MeC$_6$*H*$_4$ + N*H*) ppm; β-Isomer: δ = 1.04 (s, 9 H, C*Me*$_3$), 2.35 (s, 3 H, *p-Me*C$_6$H$_4$), 3.89 (s, 3 H, N*Me*), 5.34, 5.52 (s, 10 H, *Cp*), 5.79, 5.90 (d, AB, $^2J_{H,H}$ = 15.1 Hz, 2 H, C*H*$_2$Ph), 7.04−7.56 (m, 10 H, C$_6$*H*$_5$ + *p*-MeC$_6$*H*$_4$ + N*H*) ppm. α/β = 1.6. ^{13}C NMR (75.457 MHz, $CDCl_3$, 25 °C) α-Isomer: δ = 21.4 (*p-Me*C$_6$H$_4$), 26.9 (C*Me*$_3$), 43.7 (*C*Me$_3$), 48.9 (N*Me*), 70.8 (*C*H$_2$Ph), 88.5, 90.5 (*Cp*), 105.6, 116.7 (*C*≡*C*), 127.0−132.5 (CH *C*$_6$H$_5$ + *p*-Me*C*$_6$H$_4$), 134.2, 138.2, 142.0 (*C-ipso* Ph + *C-ipso* Tol + *C*−Me Tol), 183.6 (*C*=N), 202.4 (*C*O), 238.4 (μ-*C*O), 305.7 (μ-*C*) ppm; β-Isomer: δ = 21.8 (*p-Me*C$_6$H$_4$), 27.1 (C*Me*$_3$), 43.7 (*C*Me$_3$), 51.0 (N*Me*), 69.6 (*C*H$_2$Ph), 88.5, 90.6 (*Cp*), 105.5, 118.5 (*C*≡*C*), 127.0−132.5 (CH *C*$_6$H$_5$ + *p*-Me*C*$_6$H$_4$), 134.6, 138.2, 141.9 (*C-ipso* Ph + *C-ipso* Tol + *C*−Me Tol), 183.6 (*C*=N), 201.3 (*C*O), 239.2 (μ-*C*O), 305.8 (μ-*C*) ppm. IR (CH_2Cl_2, 25 °C): $\tilde{\nu}$ = 2201 m (C≡C), 1968 vs (CO), 1810 s (μ-CO), 1606 w, 1568 m, 1548 w, 1509 m (C=N) cm^{-1}. IR (KBr, 25 °C): $\tilde{\nu}$ = 3315 s (NH) cm^{-1}. MS (ESI): ES+ *m*/*z* = 721, ES− *m*/*z* = 149.

3c: $C_{30}H_{33}F_3N_2O_5Ru_2S$ (793.82): calcd. C 45.39, H 4.19, N 3.53; found C 45.28, H 4.23, N 3.42. Yield: 89.3 mg, 75%. ^{1}H NMR (300.04 MHz, $CDCl_3$, 25 °C): δ = 1.07 (s, 9 H, C*Me*$_3$), 2.44 (s, 3 H, *p-Me*C$_6$H$_4$), 4.05, 4.18 (s, 6 H, N*Me*$_2$), 5.34, 5.46 (s, 10 H, *Cp*), 7.03 (br., 1 H, N*H*), 7.08−7.58 (m, 4 H, *p*-MeC$_6$*H*$_4$) ppm. ^{13}C NMR (75.457 MHz, $CDCl_3$, 25 °C): δ = 21.4 (*p-Me*C$_6$H$_4$), 27.0 (C*Me*$_3$), 43.6 (*C*Me$_3$), 52.0, 53.8 (N*Me*$_2$), 88.2, 90.2 (*Cp*), 105.3, 116.8 (*C*≡*C*), 128.8, 129.7, 131.4, 132.0 (CH *p*-Me*C*$_6$H$_4$), 138.1, 141.8 (*C-ipso* + *C*−Me *p*-Me*C*$_6$H$_4$), 183.4 (*C*=N), 201.2 (*C*O), 238.7 (μ-*C*O), 303.6 (μ-*C*) ppm. IR (CH_2Cl_2, 25 °C): $\tilde{\nu}$ = 2201 m (C≡C), 1968 vs (CO), 1809 s (μ-CO), 1588 w, 1509 m (C=N) cm^{-1}. IR (KBr, 25 °C): $\tilde{\nu}$ = 3322 m (NH) cm^{-1}.

4a: $C_{36}H_{37}F_3N_2O_5Ru_2S$ (868.91): calcd. C 49.76, H 4.29, N 3.22; found C 49.22, H 4.01, N 3.58. Yield: 89.9 mg, 65%. ^{1}H NMR (300.04 MHz, $CDCl_3$, 25 °C) α-Isomer: δ = 1.15 (s, 9 H, C*Me*$_3$), 2.24, 2.44 (s, 6 H, *Me*$_2$C$_6$H$_3$), 4.41 (s, 3 H, N*Me*), 4.95, 5.45 (s, 10 H, *Cp*), 7.04 (br., 1 H, N*H*), 7.06−7.76 (m, 8 H, Me$_2$C$_6$*H*$_3$ + C$_6$*H*$_5$) ppm; β-Isomer: concentration too low to be characterized (α/β > 20:1). ^{13}C NMR (75.457 MHz, $CDCl_3$, 25 °C) α-Isomer: δ = 17.6, 18.5 (*Me*$_2$C$_6$H$_3$), 26.8 (C*Me*$_3$), 44.0 (*C*Me$_3$), 53.2 (N*Me*), 89.0, 89.9 (Cp), 105.0 120.1, (*C*≡*C*), 128.1−148.2 (Me$_2$*C*$_6$H$_3$ + *C*$_6$H$_5$), 184.2 (*C*=N), 201.5 (*C*O), 235.8 (μ-*C*O), 311.4 (μ-*C*) ppm. IR (CH_2Cl_2, 25 °C): $\tilde{\nu}$ = 2206 m (C≡C), 1969 vs (CO), 1814 s (μ-CO), 1568 w, 1525 m (C=N) cm^{-1}.

4b: $C_{35}H_{35}F_3N_2O_5Ru_2S$ (854.88): calcd. C 49.17, H 4.13, N 3.28; found C 49.55, H 4.01, N 3.60. Yield: 76.9 mg, 60%. ^{1}H NMR (300.04 MHz, $CDCl_3$, 25 °C) α-Isomer: δ = 1.08 (s, 9 H, C*Me*$_3$), 3.96 (s, 3 H, N*Me*), 5.40, 5.51 (s, 10 H, *Cp*), 5.58, 5.66 (d, AB, $^2J_{H,H}$ = 14.0 Hz, 2 H, C*H*$_2$Ph), 7.12−7.69 (m, 11 H, C$_6$*H*$_5$ + CH$_2$C$_6$*H*$_5$ + N*H*); β-Isomer: δ = 1.04 (s, 9 H, C*Me*$_3$), 3.90 (s, 3 H, N*Me*), 5.35, 5.53 (s, 10 H, *Cp*), 5.82, 5.91 (d, AB, $^2J_{H,H}$ = 14.0 Hz, 2 H, C*H*$_2$Ph), 7.12−7.69 (m, 11 H, C$_6$*H*$_5$ + CH$_2$C$_6$*H*$_5$ + N*H*) ppm. α/β = 1.9. ^{13}C NMR (75.457 MHz, $CDCl_3$, 25 °C) α-Isomer: δ = 27.0 (C*Me*$_3$), 43.8 (*C*Me$_3$), 49.0 (N*Me*), 70.9 (*C*H$_2$Ph), 88.5, 90.6 (*Cp*), 105.1, 119.8 (*C*≡*C*), 127.1−134.6 (*C*$_6$H$_5$ + CH$_2$*C*$_6$H$_5$), 183.6 (*C*=N), 202.4 (*C*O), 238.5 (μ-*C*O), 305.6 (μ-*C*); β-Isomer: δ = 26.9

(C*Me*$_3$), 43.8 (*C*Me$_3$), 51.1 (N*Me*), 69.7 (*C*H$_2$Ph), 88.5, 90.6 (*Cp*), 104.6, 119.0 (*C*≡*C*), 127.1−134.6 (C_6H_5 + $CH_2C_6H_5$), 183.6 (*C*=N), 201.3 (*C*O), 239.3 (μ-*C*O), 305.6 (μ-*C*) ppm. IR (CH_2Cl_2, 25 °C): $\tilde{\nu}$ = 2206 m (C≡C), 1966 vs (CO), 1810 s (μ-CO), 1584 w, 1570 m, 1545 w (C=N) cm^{-1}. MS (ESI): ES+ *m*/*z* = 707, ES− *m*/*z* = 149.

4c: $C_{29}H_{31}F_3N_2O_5Ru_2S$ (778.78): calcd. C 44.73, H 4.01, N 3.60; found C 44.59, H 4.13, N 3.49. Yield: 84.1 mg, 72%. ^{1}H NMR (300.04 MHz, $CDCl_3$, 25 °C): δ = 1.04 (s, 9 H, C*Me*$_3$), 4.02, 4.15 (s, 6 H, N*Me*$_2$), 5.30, 5.42 (s, 10 H, *Cp*), 7.08 (br., 1 H, N*H*), 7.44−7.68 (m, 5 H, C_6H_5) ppm. ^{13}C NMR (75.457 MHz, $CDCl_3$, 25 °C): δ = 27.0 (C*Me*$_3$), 43.7 (*C*Me$_3$), 52.1, 53.8 (N*Me*$_2$), 88.2, 90.3 (*Cp*), 104.7, 120.0 (*C*≡*C*), 129.0, 131.0, 132.1 (C_6H_5), 183. 5 (*C*=N), 201.1 (*C*O), 238.6 (μ-*C*O), 303.7 (μ-*C*) ppm. IR (CH_2Cl_2, 25 °C): $\tilde{\nu}$ = 2206 m (C≡C), 1966 vs (CO), 1807 s (μ-CO), 1591 w (C=N) cm^{-1}. IR (KBr, 25 °C): $\tilde{\nu}$ = 3317 m (NH) cm^{-1}.

5: $C_{29}H_{31}F_3N_2O_5Ru_2S$ (778.78): calcd. C 44.73, H 4.01, N 3.60; found C 4.97, H 4.11, N 3.45. Yield: 65.4 mg, 56%. ^{1}H NMR (300.04 MHz, $CDCl_3$, 25 °C) α-Isomer: δ = 0.97 (s, 9 H, C*Me*$_3$), 2.14 (s, 1 H, *H*C≡C), 3.89 (s, 3 H, N*Me*), 5.33, 5.46 (s, 10 H, *Cp*), 5.49, 5.58 (d, AB, $^2J_{H,H}$ = 14.3 Hz, 2 H, C*H*$_2$Ph), 7.16−7.38 (m, 6 H, $CH_2C_6H_5$ + N*H*) ppm; β-Isomer: δ = 0.94 (s, 9 H, C*Me*$_3$), 2.13 (s, 1 H, *H*C≡C), 3.83 (s, 3 H, N*Me*), 5.28, 5.48 (s, 10 H, *Cp*), 5.44, 5.56 (d, AB, $^2J_{H,H}$ = 13.5 Hz, 2 H, C*H*$_2$Ph), 7.16−7.38 (m, 6 H, $CH_2C_6H_5$ + N*H*) ppm. α/β = 2.1. ^{13}C NMR (75.457 MHz, $CDCl_3$, 25 °C) α-Isomer: δ = 26.6 (C*Me*$_3$), 43.8 (*C*Me$_3$), 49.3 (N*Me*), 70.9 (*C*H$_2$Ph), 88.6, 90.6 (*Cp*), 93.9 (C≡*C*H), 118.8 (*C*≡CH), 127.0−129.3 (CH $CH_2C_6H_5$), 134.1 (*C-ipso* $CH_2C_6H_5$), 183.3 (*C*=N), 202.4 (*C*O), 238.5 (μ-*C*O), 305.0 (μ-*C*) ppm; β-Isomer: δ = 26.7 (C*Me*$_3$), 44.7 (*C*Me$_3$), 51.1 (N*Me*), 70.6 (*C*H$_2$Ph), 88.6, 90.6 (*Cp*), 93.7 (C≡*C*H), 118.8 (*C*≡CH), 127.0−129.3 (CH $CH_2C_6H_5$), 134.5 (*C-ipso* $CH_2C_6H_5$), 183.3 (*C*=N), 201.4 (*C*O), 238.9 (μ-*C*O), 306.6 (μ-*C*) ppm. IR (CH_2Cl_2, 25 °C): $\tilde{\nu}$ = 1967 vs (CO), 1809 s (μ-CO), 1587 w, 1570 m, 1545 w (C=N) cm^{-1}. MS (ESI): ES+ *m*/*z* = 631, ES− *m*/*z* = 149.

6: $C_{34}H_{41}F_3N_2O_5Ru_2S$ (852.60): calcd. C 47.90, H 4.85, N 3.29; found C 48.02, H 4.71, N 3.18. Yield: 88.2 mg, 69%. ^{1}H NMR (300.04 MHz, $CDCl_3$, 25 °C) α-Isomer: δ = 0.93 (t, $^3J_{H,H}$ = 7.3 Hz, 3 H, $CH_2CH_2CH_2CH_3$), 0.98 (s, 9 H, C*Me*$_3$), 1.45, 1.66 (m, 4 H, $CH_2CH_2CH_2CH_3$), 2.09, 2.36 (s, 6 H, *Me*$_2$C$_6$H$_3$), 2.61 (t, $^3J_{H,H}$ = 7.1 Hz, 2 H, $CH_2CH_2CH_2CH_3$), 4.29 (s, 3 H, N*Me*), 4.87, 5.34 (s, 10 H, *Cp*), 7.13−7.24 (m, 4 H, $Me_2C_6H_3$ + N*H*) ppm. β-Isomer: concentration too low to be characterized (α/β > 20:1). ^{13}C NMR (75.457 MHz, $CDCl_3$, 25 °C) α-Isomer: δ = 13.6 ($CH_2CH_2CH_2CH_3$), 17.5, 18.5 (*Me*$_2$C$_6$H$_3$), 26.8 (C*Me*$_3$), 19.7, 22.3, 29.8 ($CH_2CH_2CH_2CH_3$), 43.9 (*C*Me$_3$), 53.1 (N*Me*), 88.9, 89.9 (*Cp*), 109.2, 118.7, (*C*≡*C*), 128.8, 128.9, 129.6 (CH $Me_2C_6H_3$), 131.6, 133.0 (*C*Me $Me_2C_6H_3$), 148.1 (*C-ipso* $Me_2C_6H_3$), 184.4 (*C*=N), 201.8 (*C*O), 235.7 (μ-*C*O), 311.3 (μ-*C*) ppm. IR (CH_2Cl_2, 25 °C): $\tilde{\nu}$ = 2215 m (C≡C), 1967 vs (CO), 1812 s (μ-CO), 1558 w, 1519 m, 1507 m (C=N) cm^{-1}.

7: $C_{33}H_{37}F_3N_2O_5Ru_2S$ (832.87): calcd. C 47.59, H 4.48, N 3.36; found C 47.71, H 4.37, N 3.21. Yield: 86.7 mg, 67%. ^{1}H NMR (300.04 MHz, $CDCl_3$, 25 °C) α-Isomer: δ = 1.04 (s, 9 H, C*Me*$_3$), 2.08 (s, 3 H, *Me*C=CH$_2$), 2.16, 2.39 (s, 6 H, *Me*$_2$C$_6$H$_3$), 4.35 (s, 3 H, N*Me*), 4.90, 5.39 (s, 10 H, *Cp*), 5.65, 5.75 (br., 2 H, MeC=C*H*$_2$), 7.17−7.28 (m, 3 H, $Me_2C_6H_3$), 7.44 (br., 1 H, N*H*) ppm; β-Isomer: δ = 0.99 (s, 9 H, C*Me*$_3$), 2.00 (s, 3 H, *Me*C=CH$_2$), 2.15, 2.42 (s, 6 H, *Me*$_2$C$_6$H$_3$), 4.19 (s, 3 H, N*Me*), 4.78, 5.57 (s, 10 H, *Cp*) ppm. α/β = 20. ^{13}C NMR (75.457 MHz, $CDCl_3$, 25 °C) α-Isomer: δ = 17.6, 18.5 (*Me*$_2$C$_6$H$_3$), 22.5 (*Me*C=CH$_2$), 26.8 (C*Me*$_3$), 44.0 (*C*Me$_3$), 53.2 (N*Me*), 88.9, 89.9 (*Cp*), 105.9, 124.9 (*C*≡*C*), 127.7 (MeC=*C*H$_2$), 128.8, 128.9, 129.6 (*C*−H $Me_2C_6H_3$), 132.5 (Me*C*=CH$_2$), 131.6, 132.9 (*C*−Me $Me_2C_6H_3$), 148.1 (*C-ipso* $Me_2C_6H_3$), 184.1 (*C*=N), 201.6 (*C*O), 235.5 (μ-*C*O), 311.5 (μ-*C*) ppm; β-Isomer: δ = 17.8, 18.9 (*Me*$_2$C$_6$H$_3$), 27.1 (C*Me*$_3$), 56.9 (N*Me*), 88.0, 91.1 (*Cp*) ppm. IR (CH_2Cl_2, 25 °C): $\tilde{\nu}$ = 2193 m (C≡C), 1969 vs (CO), 1814 s (μ-CO), 1566 w, 1525 m (C=N) cm^{-1}.

[Ru$_2${μ-CN(Me)(R)}(μ-CO)(CO){N(H)=C(CMe$_3$)C(H)=C(NMe$_2$)-(Tol)}(Cp)$_2$]$^+$ (R = Xy, 8a; Bz, 8b; Me, 8c). General Procedure: Me_2NH (3 mL, 2 M in THF, 6 mmol) was added to a solution of **3a**−**c** (0.1 mmol) in THF (5 mL) and stirred at room temperature for 1 hour. The solvent was removed in vacuo and the residue dissolved in CH_2Cl_2 (4 mL) and chromatographed through Al_2O_3. The final product was obtained as an orange-yellow fraction using CH_3CN as eluent.

8a: $C_{39}H_{46}F_3N_3O_5Ru_2S$ (928.02): calcd. C 50.48, H 5.00, N 4.53; found C 50.26, H 5.14, N 4.89. Yield: 56.6 mg, 61%. ^{1}H NMR (300.04 MHz, $CDCl_3$, 25 °C) α-Isomer: δ = 0.68 (s, 9 H, C*Me*$_3$), 2.22, 2.45 (s, 6 H, *Me*$_2$C$_6$H$_3$), 2.38 (s, 3 H, *p*-*Me*C$_6$H$_4$), 2.89 (s, 6 H, N*Me*$_2$), 4.31 (s, 3 H, N*Me*), 5.08 (s, 1 H, *H*C=C), 4.97, 5.36 (s, 10 H, *Cp*), 6.69 (br., 1 H, N*H*), 7.12−7.32 (m, 7 H, $Me_2C_6H_3$ + *p*-MeC_6H_4) ppm. β-Isomer: concentration too low to be characterized (α/β > 20:1). ^{13}C NMR (75.457 MHz, $CDCl_3$, 25 °C) α-Isomer: δ = 17.8, 18.5 (*Me*$_2$C$_6$H$_3$), 21.3 (*p*-*Me*C$_6$H$_4$), 29.1 (C*Me*$_3$), 41.5 (N*Me*$_2$), 42.2 (*C*Me$_3$), 58.8 (N*Me*), 88.7, 89.8 (*Cp*), 100.5 (H*C*=C), 128.8, 128.9, 129.4, 129.6, 129.7 (*C*−H $Me_2C_6H_3$ + *p*-MeC_6H_4), 131.6, 133.2, 134.1 (*C*−Me $Me_2C_6H_3$ + *p*-MeC_6H_4), 140.1, 147.8 (*C-ipso* $Me_2C_6H_3$ + *p*-MeC_6H_4), 155.4 (HC=*C*), 201.0 (*C*=N), 202.9 (*C*O), 235.8 (μ-*C*O), 311.7 (μ-*C*) ppm. IR (CH_2Cl_2, 25 °C): $\tilde{\nu}$ = 1966 vs (CO), 1809 s (μ-CO), 1600 br, 1512 m (C=N) cm^{-1}. IR (KBr, 25 °C): $\tilde{\nu}$ = 3326 br. (NH) cm^{-1}. MS (ESI): ES+ *m*/*z* = 780, ES− *m*/*z* = 149.

8b: $C_{38}H_{44}F_3N_3O_5Ru_2S$ (913.99): calcd. C 49.94, H 4.85, N 4.60; found C 49.78, H 5.12, N 4.35. Yield: 54.8 mg, 60%. ^{1}H NMR (300.04 MHz, $CDCl_3$, 25 °C) α-Isomer: δ = 0.54 (s, 9 H, C*Me*$_3$), 2.32 (s, 3 H, *p*-*Me*C$_6$H$_4$), 2.82 (s, 6 H, N*Me*$_2$), 3.84 (s, 3 H, N*Me*), 4.88 (s, 1 H, *H*C=C), 5.21, 5.48 (s, 10 H, *Cp*), 5.55, 5.64 (d, AB, $^2J_{H,H}$ = 14.2 Hz, 2 H, C*H*$_2$Ph), 6.38 (br., 1 H, N*H*), 6.99−7.33 (m, 9 H, C_6H_5 + *p*-MeC_6H_4) ppm; β-Isomer: δ = 0.50 (s, 9 H, C*Me*$_3$), 2.28 (s, 3 H, *p*-*Me*C$_6$H$_4$), 2.80 (s, 6 H, N*Me*$_2$), 3.88 (s, 3 H, N*Me*), 4.92 (s, 1 H, *H*C=C), 5.23, 5.51 (s, 10 H, *Cp*), 5.75, 5.78 (d, AB, $^2J_{H,H}$ = 16.0 Hz, 2 H, C*H*$_2$Ph), 6.42 (br., 1 H, N*H*), 6.99−7.33 (m, 9 H, C_6H_5 + *p*-MeC_6H_4) ppm. α/β = 1.8. ^{13}C NMR (75.457 MHz, $CDCl_3$, 25 °C) α-Isomer: δ = 21.3 (*p*-*Me*C$_6$H$_4$), 29.0 (C*Me*$_3$), 41.5 (N*Me*$_2$), 43.6 (*C*Me$_3$), 48.6 (N*Me*), 70.7 (*C*H$_2$Ph), 88.3, 90.4 (*Cp*), 100.2 (H*C*=C), 127.4−129.6 (CH C_6H_5 + *p*-MeC_6H_4), 134.1, 134.5, 140.1 (*C-ipso* Ph + *C-ipso* Tol + *C*−Me Tol), 155.5 (HC=*C*), 200.1 (*C*=N), 203.4 (*C*O), 237.7 (μ-*C*O), 306.4 (μ-*C*) ppm; β-Isomer: δ = 21.5 (*p*-*Me*C$_6$H$_4$), 29.1 (C*Me*$_3$), 41.5 (N*Me*$_2$), 43.7 (*C*Me$_3$), 50.9 (N*Me*), 69.6 (*C*H$_2$Ph), 88.1, 90.6 (*Cp*), 101.4 (H*C*=C), 127.4−129.6 (CH C_6H_5 + *p*-MeC_6H_4), 134.0, 134.2, 140.1 (*C-ipso* Ph + *C-ipso* Tol + *C*−Me Tol), 155.2 (HC=*C*), 200.4 (*C*=N), 202.6 (*C*O), 239.3 (μ-*C*O), 306.43 (μ-*C*) ppm. IR (CH_2Cl_2, 25 °C): $\tilde{\nu}$ = 1962 vs (CO), 1806 s (μ-CO), 1589 w, 1569 w, 1570 m, 1542 m, 1504 m (C=N) cm^{-1}. IR (KBr, 25 °C): $\tilde{\nu}$ = 3324 br. (NH) cm^{-1}.

8c: $C_{32}H_{40}F_3N_3O_5Ru_2S$ (837.89): calcd. C 45.87, H 4.81, N 5.01; found C 46.13, H 4.65, N 5.33. Yield: 58.7 mg, 70%. ^{1}H NMR (300.04 MHz, $CDCl_3$, 25 °C): δ = 0.62 (s, 9 H, C*Me*$_3$), 2.37 (s, 3 H, *p*-*Me*C$_6$H$_4$), 2.85 (s, 6 H, N*Me*$_2$), 4.03, 4.09 (s, 6 H, μ-CN*Me*$_2$), 4.89 (s, 1 H, *H*C=C), 5.17, 5.46 (s, 10 H, *Cp*), 6.45 (br., 1 H, N*H*), 7.08−7.32 (m, 4 H, *p*-MeC_6H_4) ppm. ^{13}C NMR (75.457 MHz,

$CDCl_3$, 25 °C): δ = 21.2 (*p*-*Me*C_6H_4), 28.9 (C*Me*$_3$), 41.3 (N*Me*$_2$), 43.5 (*C*Me$_3$), 51.6, 53.5 (μ-CN*Me*$_2$), 87.8, 90.0 (*Cp*), 99.9 (H*C*=C), 129.2, 129.5 (CH *p*-Me*C*$_6H_4$), 133.8 (*C*−Me *p*-Me*C*$_6H_4$), 140.0 (*C*-*ipso* *p*-Me*C*$_6H_4$), 155.2 (HC=*C*), 200.0 (*C*=N), 202.4 (*C*O), 238.1 (μ-*C*O), 304.8 (μ-*C*) ppm. IR (CH_2Cl_2, 25 °C): $\tilde{\nu}$ = 1964 vs (CO), 1806 s (μ-CO), 1588 w, 1559 m, 1510 m (C=N) cm^{-1}. IR (KBr, 25 °C): $\tilde{\nu}$ = 3326 br. (NH) cm^{-1}.

[Ru$_2${μ-CN(Me)(Xy)}(μ-CO)(CO){N(H)=C(CMe$_3$)C(H)=C-(NC$_5$H$_{10}$)(Tol)}(Cp)$_2$]$^+$ (9): $C_5H_{10}NH$ (0.6 mL, 5.1 mmol) was added to a solution of **3a** (88.5 mg, 0.1 mmol) in THF (5 mL) and stirred at room temperature for 1 h. The solvent was removed in vacuo and the residue dissolved in CH_2Cl_2 (4 mL) and chromatographed through Al_2O_3. The final product was obtained as an orange-yellow fraction using CH_3CN as eluent.

$C_{42}H_{50}F_3N_3O_5Ru_2S$ (968.08): calcd. C 52.11, H 5.21, N 4.34; found C 52.35, H 5.23, N 4.68. Yield: 67.8 mg, 70%. ^{1}H NMR (300.04 MHz, $CDCl_3$, 25 °C) α-Isomer: δ = 0.67 (s, 9 H, C*Me*$_3$), 1.69 (m, 6 H, β- + γ-C*H*$_2$ C_5H_{10}), 2.22, 2.44 (s, 6 H, *Me*$_2$C$_6$H$_3$), 2.38 (s, 3 H, *p*-*Me*C$_6$H$_4$), 3.11 (br., 4 H, α-C*H*$_2$ C_5H_{10}), 4.29 (s, 3 H, N*Me*), 5.20 (s, 1 H, *H*C=C), 4.98, 5.38 (s, 10 H, *Cp*), 6.67 (br., 1 H, N*H*), 7.08−7.32 (m, 7 H, Me$_2$C$_6$*H*$_3$ + *p*-MeC$_6$*H*$_4$) ppm; β-Isomer: δ = 0.56 (s, 9 H, C*Me*$_3$), 4.27 (s, 3 H, N*Me*), 4.75, 5.64 (s, 10 H, *Cp*) ppm. α/β = 20. ^{13}C NMR (75.457 MHz, $CDCl_3$, 25 °C) α-Isomer: δ = 17.8, 18.5 (*Me*$_2$C$_6$H$_3$), 21.4 (*p*-*Me*C$_6$H$_4$), 24.8 (γ-*C*H$_2$ C_5H_{10}), 26.6 (β-*C*H$_2$ C_5H_{10}), 29.0 (C*Me*$_3$), 44.2 (*C*Me$_3$), 50.8 (α-*C*H$_2$ C_5H_{10}), 52.9 (N*Me*), 88.6, 89.8 (*Cp*), 101.8 (H*C*=C), 128.8−130.1 (*C*−H Me$_2$C$_6$H$_3$ + *p*-MeC$_6$H$_4$), 133.2, 136.7, 137.8, (*C*−Me Me$_2$C$_6$H$_3$ + *p*-Me*C*$_6$H$_4$), 140.1, 147.8 (*C*-*ipso* Me$_2$*C*$_6$H$_3$ + *p*-Me*C*$_6$H$_4$), 156.0 (HC=*C*), 201.5 (*C*=N), 202.9 (*C*O), 235.9 (μ-*C*O), 311.7 (μ-*C*) ppm; β-Isomer: δ = 28.7 (C*Me*$_3$), 87.4, 91.0 (*Cp*) ppm. IR (CH_2Cl_2, 25 °C): $\tilde{\nu}$ = 1965 vs (CO), 1810 s (μ-CO), 1593 w, 1514 m (C=N) cm^{-1}. IR (KBr, 25 °C): $\tilde{\nu}$ = 3326 br. (NH) cm^{-1}. MS (ESI): ES+ *m*/*z* = 820, ES− *m*/*z* = 149.

[Ru$_2${μ-CN(Me)(Xy)}(μ-CO)(CO){N(H)=C(CMe$_3$)C(H)=C-(NMe$_2$)[C(Me)=CH$_2$)}(Cp)$_2$]$^+$ (10): Me_2NH (3 mL, 2 M in THF, 6 mmol) was added to a solution of **7** (100.0 mg, 0.120 mmol) in THF (6 mL) and stirred at room temperature for 1 hour. The solvent was removed in vacuo and the residue dissolved in CH_2Cl_2 (4 mL) and chromatographed through Al_2O_3. The final product was obtained as an orange-yellow fraction using CH_3CN as eluent.

$C_{35}H_{44}F_3N_3O_5Ru_2S$ (877.96): calcd. C 47.88, H 5.05, N 4.79; found C 47.56, H 5.41, N 4.52. Yield: 36.7 mg, 52%. ^{1}H NMR (300.04 MHz, $CDCl_3$, 25 °C) α-Isomer: δ = 0.96 (s, 9 H, C*Me*$_3$), 1.19 (s, 3 H, *Me*C=), 2.23, 2.43 (s, 6 H, *Me*$_2$C$_6$H$_3$), 2.85 (s, 6 H, N*Me*$_2$), 4.26 (s, 3 H, N*Me*), 4.92 (s, 1 H, *H*C=C), 4.96, 5.34 (s, 10 H, *Cp*), 5.19, 5.22 (br., 2 H, =C*H*$_2$), 6.53 (br., 1 H, N*H*), 7.21−7.30 (m, 3 H, Me$_2$C$_6$*H*$_3$ + *p*-MeC$_6$*H*$_4$) ppm; β-Isomer: concentration too low to be characterized (α/β > 20:1). ^{13}C NMR (75.457 MHz, $CDCl_3$, 25 °C) α-Isomer: δ = 17.7, 18.4 (*Me*$_2$C$_6$H$_3$), 21.5 (*Me*C=), 29.5 (C*Me*$_3$), 40.9 (N*Me*$_2$), 44.2 (*C*Me$_3$), 52.8 (N*Me*), 88.5, 89.8 (*Cp*), 100.2 (H*C*=C), 122.2 (=*C*H$_2$), 128.9, 129.0, 129.6 (*C*−H Me$_2$C$_6$H$_3$), 131.5, 133.2 (*C*−Me Me$_2$C$_6$H$_3$), 142.3 (Me*C*=CH$_2$), 147.8 (*C*-*ipso* Me$_2$*C*$_6$H$_3$), 156.6 (HC=*C*), 201.2 (*C*=N), 202.9 (*C*O), 236.1 (μ-*C*O), 312.2 (μ-*C*) ppm. IR (CH_2Cl_2, 25 °C): $\tilde{\nu}$ = 1967 vs (CO), 1810 s (μ-CO), 1593 w, 1516 m (C=N) cm^{-1}.

X-ray Crystallographic Study: Compounds **3a[CF$_3$SO$_3$]** and **8a[CF$_3$SO$_3$]** were crystallized from CH_2Cl_2/Et_2O. Crystal data were collected at room temperature on a Bruker AXS SMART 2000 CCD diffractometer using Mo-K_α radiation. Intensity data were measured over full diffraction spheres using 0.3° wide ω scans, crystal-to-detector distance 5.2 cm. Cell dimensions and orientation

Table 3. Crystal data and experimental details for **3a[CF$_3$SO$_3$]** and **10a[CF$_3$SO$_3$]**

Complex	**3a[CF$_3$SO$_3$]**	**8a[CF$_3$SO$_3$]**
Empirical formula	$C_{37}H_{39}F_3N_2O_5Ru_2S$	$C_{39}H_{46}F_3N_3O_5Ru_2S$
Formula mass	882.90	927.99
T, K	293(2)	293(2)
λ, Å	0.71073	0.71073
Crystal system	orthorhombic	monoclinic
Space group	$P2_12_12_1$	Cc
a, Å	12.245(2)	12.925(3)
b, Å	14.179(3)	24.789(5)
c, Å	22.219(4)	26.031(5)
α, °	90	90
β, °	90	96.43(3)
γ, °	90	90
Cell volume, Å^3	3857.7(13)	8288(3)
Z	4	8
$D_{calcd.}$, g·cm^{-3}	1.520	1.487
μ, mm^{-1}	0.894	0.836
F(000)	1784	3776
Crystal size, mm	0.35 × 0.25 × 0.19	0.28 × 0.22 × 0.15
θ limits, °	1.70−25.03	1.57−25.03
Reflections collected	34166	36307
Independent reflections	6830 [*R*(int) = 0.0617]	14605 [*R*(int) = 0.1155]
Data/restraints/parameters	6830/ 211/417	14605/554/778
Goodness on fit on F^2	1.075	0.934
*R*1 [$I > 2\sigma(I)$]	0.0661	0.0725
*wR*2 (all data)	0.1756	0.1940
Largest diff. peak and hole, e·Å^{-3}	3.835/−0.837	1.094/−1.154

matrices were initially determined from least-squares refinements on reflections measured in 3 sets of 20 exposures collected in three different ω regions and eventually refined against all reflections. The software SMART [28] was used for collecting frames of data, indexing reflections and determination of lattice parameters. The collected frames were then processed for integration by the software SAINT and empirical absorption corrections were applied with SADABS.[29] Structures were solved by direct methods and structures refined by full-matrix least-squares based on all data using F^2.[30] Crystal data are listed in Table 3. Non-H atoms were refined anisotropically, unless otherwise stated. The hydrogen atoms were added in idealized positions except the ones attached to nitrogen atoms in **8a[CF_3SO_3]** which were located in the Fourier map and refined isotropically with isotropic thermal parameters defined as $U(H) = 1.2U_{eq}(N)$. The crystals of both **3a[CF_3SO_3]** and **8a[CF_3SO_3]** appeared to be racemically twinned with a refined Flack parameter of 0.47(7) and 0.41(7), respectively.[31] They were, therefore, refined using the TWIN refinement routine of SHELXTL. Some residual electron density peaks up to 3.835 e·Å^{-3} remain after refinement of **3a[CF_3SO_3]**, probably because of partial non-merohedral twinning. Different crystals of **3a[CF_3SO_3]** have been examined, and we have also tried to recrystallize them, without obtaining better results. Nonetheless, the data are fully consistent with the ones previously reported for the analogous complex [Fe_2{μ-CN(Me)(Xy)}(μ-CO)(CO){N(H)=C(CMe_3)(C≡CTol)}-$(Cp)_2$][CF_3SO_3].[10] One Cp ligand and the CMe_3 group in the unique molecule of **8a[CF_3SO_3]** are both disordered. Disordered atomic positions were split and refined isotropically using similar distance and similar U restraints and one occupancy parameter per disordered group.

CCDC-222309 and -222310 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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