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Journal of Organometallic Chemistry 691 (2006) 2424–2439
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

New diruthenium vinyliminium complexes from the insertion of alkynes into bridging aminocarbynes

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Received 19 December 2005; received in revised form 11 January 2006; accepted 11 January 2006
Available online 23 February 2006

Abstract

Primary alkynes R′C≡CH [R′ = Me_3Si, Tol, CH_2OH, CO_2Me, $(CH_2)_4C{\equiv}CH$, Me] insert into the metal–carbon bond of diruthenium μ-aminocarbynes [Ru_2{μ-CN(Me)(R)}(μ-CO)(CO)(MeCN)$(Cp)_2$][SO_3CF_3] [R = 2,6-$Me_2C_6H_3$ (Xyl), **1a**; CH_2Ph (Bz), **1b**; Me, **1c**] to give the vinyliminium complexes [Ru_2{μ-η^1:η^3-C(R′)=CHC=N(Me)(R)}(μ-CO)(CO)$(Cp)_2$][SO_3CF_3] [R = Xyl, R′ = Me_3Si, **2a**; R = Bz, R′ = Me_3Si, **2b**; R = Me, R′ = Me_3Si, **2c**; R = Xyl, R′ = Tol, **3a**; R = Bz, R′ = Tol, **3b**; R = Bz, R′ = CH_2OH, **4**; R = Bz, R′ = CO_2Me, **5a**; R = Me, R′ = CO_2Me, **5b**; R = Xyl, R′ = $(CH_2)_4C{\equiv}CH$, **6**; R = Xyl, R′ = Me, **7a**; R = Bz, R′ = Me, **7b**; R = Me, R′ = Me, **7c**]. The related compound [Ru_2{μ-η^1:η^3-C[C(Me)=CH_2]=CHC=N(Me)(Xyl)}(μ-CO)(CO)$(Cp)_2$][SO_3CF_3], (**9**) is better prepared by reacting [Ru_2{μ-CN(Me)(Xyl)}(μ-CO)(CO)(Cl)$(Cp)_2$] (**8**) with $AgSO_3CF_3$ in the presence of HC≡CC(Me)=CH_2 in CH_2Cl_2 at low temperature. In a similar way, also secondary alkynes can be inserted to give the new complexes [Ru_2{μ-η^1:η^3-C(R′)=C(R′)C=N(Me)(R)}(μ-CO)(CO)$(Cp)_2$][SO_3CF_3] (R = Bz, R′ = CO_2Me, **11**; R = Xyl, R′ = Et, **12a**; R = Bz, R′ = Et, **12b**; R = Xyl, R′ = Me, **13**). The reactions of **2–7**, **9**, **11–13** with hydrides (i.e., $NaBH_4$, NaH) have been also studied, affording μ-vinylalkylidene complexes [Ru_2{μ-η^1:η^3-C(R′)C(R″)=C(H)N(Me)(R)}(μ-CO)(CO)$(Cp)_2$] (R = Bz, R′ = Me_3Si, R″ = H, **14a**; R = Me, R′ = Me_3Si, R″ = H, **14b**; R = Bz, R′ = Tol, R″ = H, **15**; R = Bz, R′ = R″ = Et, **16**), bis-alkylidene complexes [Ru_2{μ-η^1:η^2-C(R′)C(H)(R″)CN(Me)(Xyl)}(μ-CO)(CO)$(Cp)_2$] (R′ = Me_3Si, R″ = H, **17**; R′ = R″ = Et, **18**), acetylide compounds [Ru_2{μ-CN(Me)(R)}(μ-CO)(CO)(C≡CR′)$(Cp)_2$] (R = Xyl, R′ = Tol, **19**; R = Bz, R′ = Me_3Si, **20**; R = Xyl, R′ = Me, **21**) or the tetranuclear species [Ru_2{μ-η^1:η^2-C(Me)CCN(Me)(Bz)}(μ-CO)(CO)$(Cp)_2$]$_2$ (**23**) depending on the properties of the hydride and the substituents on the complex. Chromatography of **21** on alumina results in its conversion into [Ru_2{μ-η^3:η^1-C[N(Me)(Xyl)]C(H)C=CH_2}(μ-CO)(CO)$(Cp)_2$] (**22**). The crystal structures of **2a**[CF_3SO_3]·0.5CH_2Cl_2, **12a**[CF_3SO_3] and **22** have been determined by X-ray diffraction studies.

Keywords: Vinyliminium; Diruthenium complexes; Alkyne insertion; Vinylalkylidene; Hydride addition

1. Introduction

We have recently reported the synthesis of diiron complexes of the type [Fe_2{μ-η^1:η^3-C_γ(R′)=C_β(R″)C_α=N(Me)(R)}(μ-CO)(CO)$(Cp)_2$][SO_3CF_3] [1], which contain a bridging vinyliminium ligand in an unusual μ-η^1:η^3 coordination mode [2]. These complexes were obtained by alkyne insertion into the metal–carbon bond of diiron μ-aminocarbynes [Fe_2{μ-CN(Me)(R)}(μ-CO)(CO)(MeCN)$(Cp)_2$][SO_3CF_3], and represent an interesting example of C–C bond formation in dinuclear μ-carbyne complexes [3]. Studies on the reactivity of the bridging vinyliminium ligand have evidenced its electrophilic character and have shown that hydride (from $NaBH_4$) can selectively add to either the C_α or the C_β of the bridging ligand, depending on the steric and electronic properties of the ligand substituents (R, R′ and R″) [4]. Moreover, it has been shown that the C_β-H hydrogen, when present, is acidic and can be easily removed upon treatment with NaH. Proton removal generates unstable intermediate species which afford, upon rearrangement, mono- and polynuclear iron complexes [5]. In order to

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doi:10.1016/j.jorganchem.2006.01.020

extend our investigation and, in particular, with the aim of understanding the role of the metal in all these reactions, we report, here, on the synthesis, characterisation and reactivity of new diruthenium vinyliminium complexes.

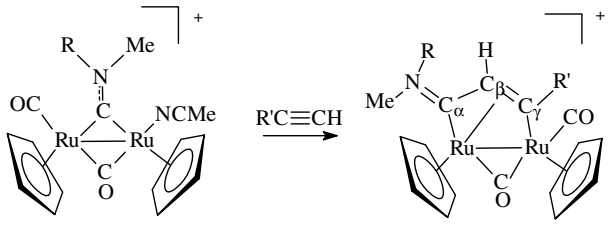
2. Results and discussion

2.1. Insertion of primary and secondary alkynes

Since alkyne insertion, in dinuclear complexes, usually requires photolysis or the presence of a labile ligand, as equivalent of a vacant coordination site, the reactions have been performed on the acetonitrile complexes $[Ru_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)(MeCN)(Cp)_2][SO_3CF_3]$ [R = 2,6-$Me_2C_6H_3$ (Xyl), **1a**; CH_2Ph (Bz), **1b**; Me, **1c**], whose synthesis is detailed in the experimental part. Complexes **1a–c** react with R′C≡CH [R′ = Me_3Si, Tol, CH_2OH, CO_2Me, $(CH_2)_4C{\equiv}CH$] in refluxing THF affording the new vinyliminium compounds $[Ru_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C(R')=CHC=N(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ [R = Xyl, R′ = Me_3Si, **2a**; R = Bz, R′ = Me_3Si, **2b**; R = Me, R′ = Me_3Si, **2c**; R = Xyl, R′ = Tol, **3a**; R = Bz, R′ = Tol, **3b**; R = Bz, R′ = CH_2OH, **4**; R = Bz, R′ = CO_2Me, **5a**; R = Me, R′ = CO_2Me, **5b**; R = Xyl, R′ = $(CH_2)_4C{\equiv}CH$, **6**] (Scheme 1).

For the reaction with volatile alkynes different approaches have been adopted. Thus, in the case of propyne, **1** has been reacted overnight at room temperature with a large excess of the alkyne, whereas the insertion of $HC{\equiv}CC(Me)=CH_2$ has been obtained from $[Ru_2\{\mu\text{-}CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cl)(Cp)_2]$ (**8**) and $AgSO_3CF_3$ in the presence of the alkyne. These procedures led to the formation of the complexes $[Ru_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C(Me)=CHC=N(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (R = Xyl, **7a**; Bz, **7b**; Me, **7c**), and $[Ru_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C[C(Me)=CH_2]=CHC=N(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (**9**) (Scheme 2).

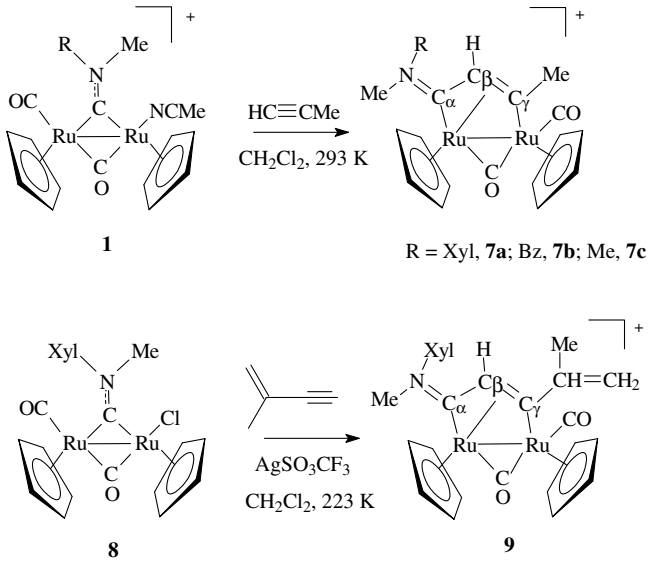
As previously reported for diiron complexes, the insertion of the primary alkynes into the Ru–C bond of the bridging aminocarbyne is completely regioselective, affording the products containing the CH unit in the β-position [1]. Accordingly, the CH proton in the ^1H spectrum resonates at 4.6–6 ppm, as expected for $C_\beta H$ [1,6]. The ^{13}C NMR spectra of **2–7**,**9** show two resonances at high frequencies due to the terminal and bridging carbonyls and distinct resonances for the two inequivalent Cp ligands. The three carbons of the vinyl iminium ligand resonate in typical regions, i.e., 216–222 ppm C_α, 53–63 ppm C_β and 175–195 ppm C_γ. The IR spectra show bands at ν(CO) ca. 1990–2000 and 1815–1825 cm^{-1} for the terminal and bridging carbonyls, respectively, and ν(C=N) at 1630–1680 cm^{-1} for the iminium group. A band at 2118 cm^{-1} in the IR spectrum of **6** is attributable to the free C≡C group. It is noteworthy that the carbonyl bands for the complexes containing the Xyl group on the vinyliminium ligand (i.e., **2a**, **3a**, **6**, **7a**, **9**) absorbs at higher frequencies compared to those of the complexes containing the Bz or Me groups, whereas the iminium group absorbs at lower frequencies. This is the consequence of the more acidic character of the Xyl.



R = Xyl, **1a**; Bz, **1b**; Me, **1c**

R	R′	
Xyl	$SiMe_3$	**2a**
Bz	$SiMe_3$	**2b**
Me	$SiMe_3$	**2c**
Xyl	Tol	**3a**
Bz	Tol	**3b**
Bz	CH_2OH	**4**
Bz	CO_2Me	**5a**
Me	CO_2Me	**5b**
Xyl	$(CH_2)_4CCH$	**6**

Scheme 1.



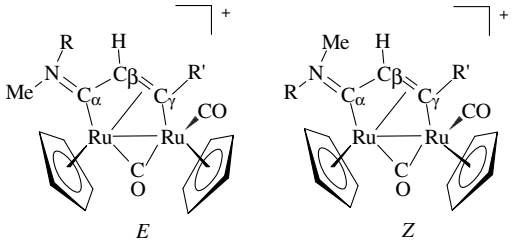
1 R = Xyl, **7a**; Bz, **7b**; Me, **7c**

8 **9**

Scheme 2.

The NMR spectra of all complexes **2–7**, **9** except **2c**, **5b** and **7b**, show the presence, in solution, of two isomers in the ratio 1.1–1.7:1 for the ones containing the Bz group and 5–10:1 when the Xyl group is present. The two isomeric forms are due to the different orientation of the substituents on the iminium group, and can be labelled *E* and *Z* (see Scheme 3) [1]. In perfect agreement, only one species is present in the case of the symmetrically substituted vinyliminium complexes **2c**, **5b** and **7b**.

The *E* and *Z* isomer can be easily distinguished on the basis of the NMe resonance in the ^1H NMR spectrum. Thus, for the Bz-containing species, the NMe group resonates at 3.4–3.9 ppm for the *E* isomer and at ca. 3.0–3.2 ppm for the *Z* isomer, whereas they resonate at ca. 4.0 (*E* isomer) and 3.5–3.7 ppm (*Z* isomer) in the case of the species with the Xyl group. The analysis of the ^1H



Scheme 3.

NMR spectra clearly indicates that the *E* isomer is the predominant species when the bulky Xyl group is present, whereas the concentration of the *E* and *Z* isomers is similar in the case of the less bulky Bz substituent. Further support to these conclusions comes from DPFGSE-NOE [7] and bidimensional NOESY studies [8]. For instance, the NOESY spectrum of **2a** shows, for the major isomer, cross peaks between the two Cp ligands, the NMe and one Cp, $C_\beta H$ and the Xyl protons, clearly confirming that the two Cp ligands are in mutual *cis* position and the NMe group points towards one Cp ligand (*E* isomer). Conversely, the NOESY spectrum shows cross peaks in between the two Cp ligands and between $C_\beta H$ and NMe for the minor isomer, which, thus, adopts a *cis*-*Z* form. A *cis*-*E* structure is also adopted by **2a** in the solid state, as shown by single crystal X-ray analysis. Thus, the molecular structure of **2a** is reported in Fig. 1, whereas the main bond lengths and bond angles are reported in Table 1. The structure of **2a** is equivalent to that previously reported for the analogous diiron complex $[Fe_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C(SiMe_3){=}CHC{=}N(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2]^+$ (**10**) and also in this case it can be discussed with reference to three different resonance forms (Scheme 4). The C(13)–C(14) [1.404(9) Å] and C(14)–C(15) [1.430(9) Å] interactions appear to be significantly different, whereas they are almost identical in **10** [1.412(8) and 1.406(8) Å, respectively], suggesting an even greater contribution in **2a** for the vinyliminium form (A in Scheme 4) than the keteniminium form (C). In agreement, also the N(1)–C(15) interaction in **2a** [1.302(8) Å] shows a greater double bond character than in **10** [1.320(7) Å]. The Ru(1)–C(13) [2.183(6) Å] and Ru(1)–C(14) [2.189(7) Å] interactions are identical within experimental errors, whereas Ru(1)–C(15) [1.955(6) Å] is considerably shorter indicating some double bond character in agreement with form B.

In general, interconversion between the *E* and *Z* forms has not been observed for any of the Ru-species described in this paper neither for the analogous iron complexes previously reported [1]. The only exception seems to be compound **6**, which is obtained, by insertion of $HC{\equiv}C(CH_2)_4C{\equiv}CH$, as a *E Z* mixture (10:1). The *E* isomer is converted into the Z form by treatment with an excess of Me_2NH, as clearly shown by NMR spectroscopy. As expected, the NMe protons resonate at 3.90 ppm in *E*-**6** and at 3.61 ppm in *Z*-**6**. Moreover, before addition of Me_2NH, irradiation of $C_\beta H$ results in the enhancement of the resonances due to the Xyl

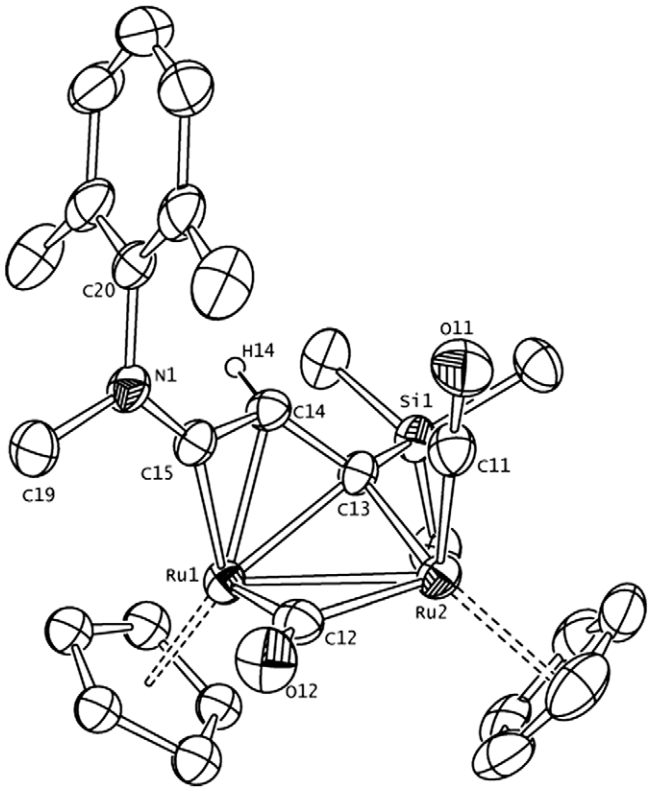


Fig. 1. Molecular structure of **2a**, with key atoms labelled (all H atoms, apart from H(14) have been omitted). Displacement ellipsoids are at 30% probability level. Only the main image of the disordered Cp ligand bound to Ru(1) is drawn.

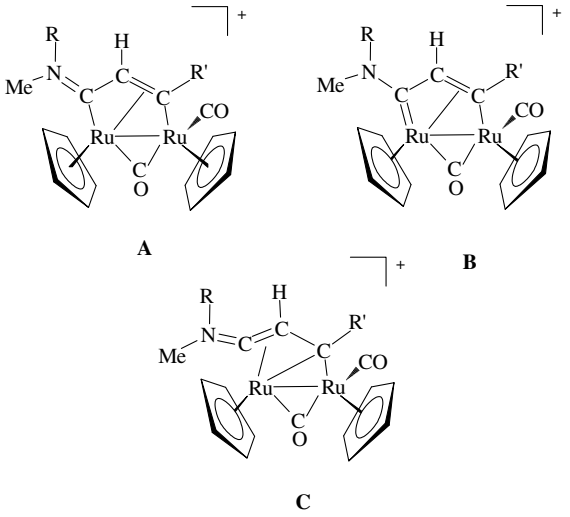
Table 1
Selected bond lengths (Å) and angles (°) for complex **2a**

Ru(1)–Ru(2)	2.729(47)	C(11)–O(11)	1.144(9)
Ru(1)–C(12)	2.062(7)	C(12)–O(12)	1.170(8)
Ru(2)–C(12)	1.996(7)	C(13)–Si(1)	1.901(6)
Ru(2)–C(11)	1.849(8)	C(13)–C(14)	1.404(9)
Ru(1)–C(13)	2.183(6)	C(14)–C(15)	1.430(9)
Ru(2)–C(13)	2.080(6)	N(1)–C(15)	1.302(8)
Ru(1)–C(14)	2.189(7)	N(1)–C(19)	1.456(9)
Ru(1)–C(15)	1.955(6)	N(1)–C(20)	1.452(9)
Ru(2)–C(13)–C(14)	121.5(5)	C(15)–N(1)–C(19)	120.6(6)
C(13)–C(14)–C(15)	120.5(6)	C(15)–N(1)–C(20)	121.2(5)
C(14)–C(15)–Ru(1)	78.9(4)	C(19)–N(1)–C(20)	117.8(5)
C(14)–C(15)–N(1)	134.2(6)		

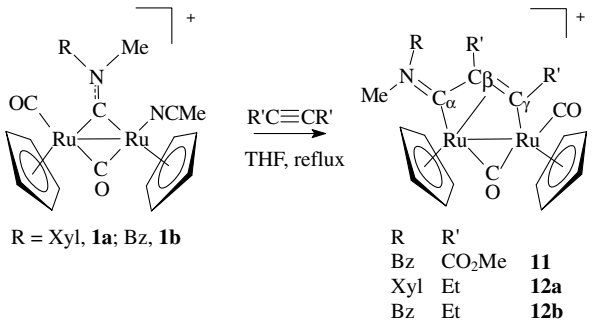
group (*E* isomer), whereas NOE is generated between $C_\beta H$ and NMe after isomerisation (*Z* isomer). The peculiar behaviour of **6** suggests that the presence of functional groups in the γ-position of the ligand can play an important role in the stereochemistry of these vinyliminium complexes.

In this sense, it is noteworthy that in the case of **9**, which is obtained by insertion of $HC{\equiv}CC(Me){=}CH_2$ into **8** at low temperature in the presence of $AgSO_3CF_3$, the *Z* and not the *E* isomer is mainly obtained.

Following the same procedure described above, it is also possible to insert disubstituted alkynes into **1** (Scheme 5). Thus, complexes $[Ru_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C(R'){=}C(R')C{=}N(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (R = Bz, R′ = CO_2Me, **11**;



Scheme 4.



Scheme 5.

R = Xyl, R′ = Et, **12a**; R = Bz, R′ = Et, **12b**) have been obtained by reacting **1a**,**b** in THF with R′C≡CR′ (R′ = CO_2Me, Et).

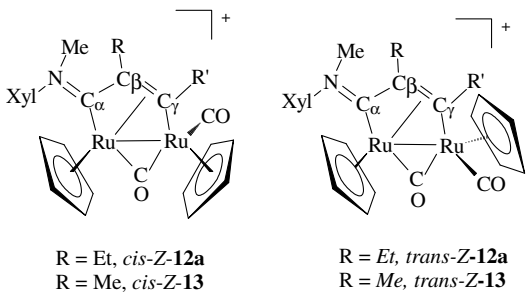
The analogous compound [Ru_2\{μ-η^1:η^3-C(Me)=C(Me)C=N(Me)(Xyl)\}(μ-CO)(CO)(Cp)$_2$][SO_3CF_3] (**13**) was obtained, instead, from [Ru_2\{μ-CN(Me)(Xyl)\}(μ-CO)(CO)(Cl)(Cp)$_2$] (**8**) and $AgSO_3CF_3$ in the presence of the volatile 2-butyne in CH_2Cl_2 at low temperature.

The IR spectra of **11**–**13**, in CH_2Cl_2, show bands in the typical regions for terminal and bridging carbonyls (1980–2000 and 1816–1838 cm^{-1}, respectively) together with a band at 1616–1670 cm^{-1} attributable to the C=N iminium group; moreover, an intense band at 1737 cm^{-1} is present in the spectrum of **11**, due to CO_2Me. It is noteworthy the fact that the presence of two strong electron withdrawing CO_2Me groups causes a shift to higher frequencies of both *ν*(CO) in **11** (i.e., 2004 and 1838 cm^{-1}) compared to **12b** (i.e., 1986 and 1816 cm^{-1}). The NMR spectra of **11**–**13** show resonances fully consistent with their nature of vinyliminium complexes (see Section 4). Their stereochemistry requires some further comments. As in the case of analogous diiron complexes [1], several isomers are observed due to either the orientation of the N substituents (*E*, *Z* isomers) and the relative position of the Cp ligands (*cis*, *trans* isomers). In particular, two isomers are present in solution in the case of the Bz-containing complexes **11** and **12b** in ratio ca. 2:1, which are attributable to the *E* and *Z* isomers. In agreement with this, the NMe protons for the *E* isomer of **11** and **12b** resonate at 3.5–3.9 ppm whereas they resonate at 3.0–3.2 ppm for the *Z* isomer. Conversely, both the isomers of **12a** and **13** show NMe resonances in the ^{1}H NMR spectra at 3.5–3.7 ppm as expected for a *Z* structure in a species containing the Xyl substituent. Thus, they can be formulated as *cis*-*Z*-**12a**, *trans*-*Z*-**12a**, *cis*-*Z*-**13** and *trans*-*Z*-**13** (see Scheme 6) similarly to what previously reported for the analogous diiron complexes [Fe_2\{μ-η^1:η^3-C(R′)=C(R′)C=N(Me)(Xyl)\}(μ-CO)(CO)(Cp)$_2$][SO_3CF_3] (R′ = Me, Et) [1].

The *cis*-*Z*-isomer seems to be the thermodynamic product, whereas the *trans*-*Z*-isomer is the kinetic one. Thus, insertion of 3-hexyne and 2-butyne into **8** at low temperature in the presence of $AgSO_3CF_3$ results mainly in the formation of *trans*-*Z*-**12a** (*trans*:*cis* = 5) and *trans*-*Z*-**13** (*trans*:*cis* = 1.3), respectively; complete isomerisation of *trans*-*Z*-**12a** and *trans*-*Z*-**13** into *cis*-*Z*-**12a** and *cis*-*Z*-**13** is, then, achieved after heating at reflux temperature in THF for 5 h. The molecular structure of *cis*-*Z*-**12a** is shown in Fig. 2, whereas the main bond lengths and bond angles are reported in Table 2. A comparison of the data of *cis*-*Z*-**12a** (Table 2) and *E*-**2a** (Table 1) shows that the observed different geometries (*E*–*Z*) and the presence of different groups on the vinyliminium ligand have no effect on all the listed bond distances.

2.2. Reactions of the diruthenium vinyliminium complexes with $NaBH_4$

As previously mentioned, investigations on the reactivity of diiron μ-vinyliminium complexes have evidenced that hydride (from $NaBH_4$) can add selectively to either the C_α or the C_β. In particular, hydride addition occurs selectively at the C_α position, except when the presence of the sterically demanding Xyl group inhibits attack in that position and directs the addition to the C_β. Addition at the C_α generates neutral complexes which can be appropriately described as bridging vinylalkylidenes. Conversely, attack at the C_β produces bis-alkylidene ligands, anchored to the Fe–Fe through the C_α and C_γ, which assume the nature of amino carbene and bridging alkylidene, respectively [4].



Scheme 6.

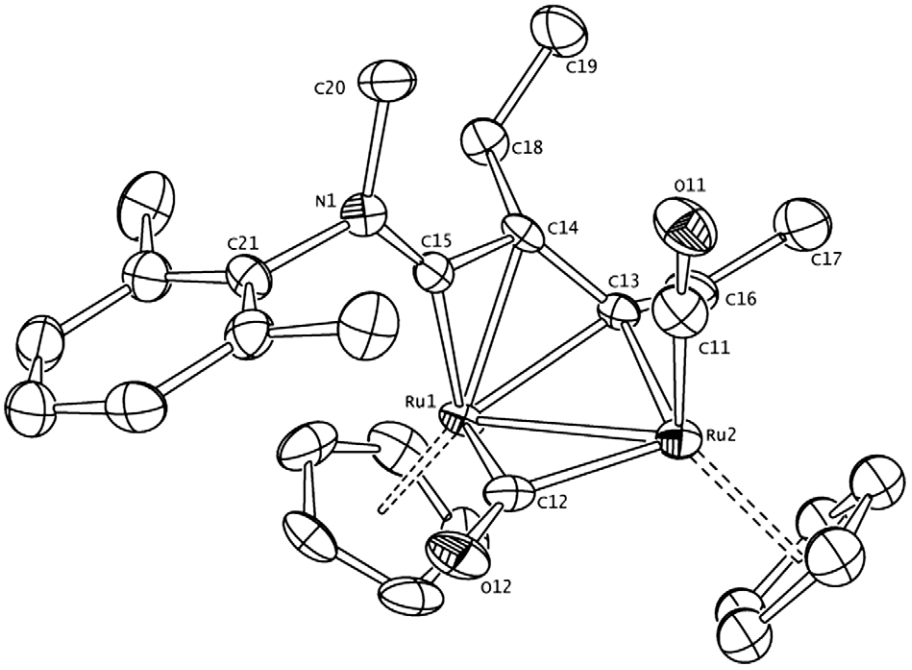


Fig. 2. Molecular structure of *cis-Z*-**12a**, with key atoms labelled (all H atoms have been omitted). Displacement ellipsoids are at 30% probability level. Only the main image of the disordered Cp ligand bound to Ru(2) is drawn.

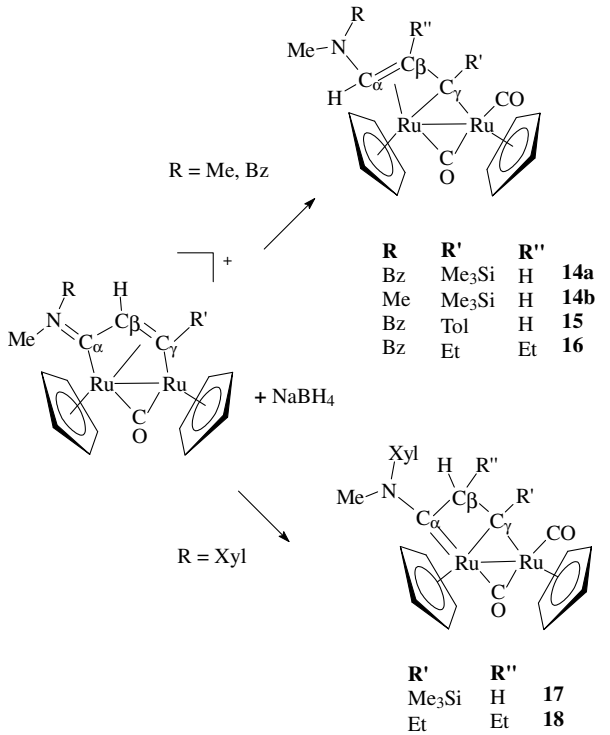
Table 2
Selected bond lengths (Å) and angles (°) for complex *cis-Z*-**12a**

Ru(1)–Ru(2)	2.7343(13)	C(11)–O(11)	1.156(11)
Ru(1)–C(12)	2.052(8)	C(12)–O(12)	1.165(9)
Ru(2)–C(12)	2.001(9)	C(13)–C(16)	1.501(11)
Ru(2)–C(11)	1.858(10)	C(13)–C(14)	1.424(11)
Ru(1)–C(13)	2.165(8)	C(14)–C(18)	1.518(11)
Ru(2)–C(13)	2.098(8)	C(14)–C(15)	1.454(11)
Ru(1)–C(14)	2.220(7)	N(1)–C(15)	1.291(10)
Ru(1)–C(15)	1.962(8)	N(1)–C(20)	1.479(10)
		N(1)–C(21)	1.476(10)
Ru(2)–C(13)–C(14)	122.4(5)	C(15)–N(1)–C(20)	121.7(7)
C(13)–C(14)–C(15)	114.5(7)	C(15)–N(1)–C(21)	119.9(7)
C(14)–C(15)–Ru(1)	79.6(5)	C(20)–N(1)–C(21)	118.3(6)
C(14)–C(15)–N(1)	133.1(7)		

Thus, the reactivity of the diruthenium vinyliminium complexes with $NaBH_4$ has been studied.

Addition of $NaBH_4$ to the diruthenium vinyliminium complexes containing Bz or Me substituents on the iminium group results in the selective addition of H^- to the C_α affording new bridging vinylalkylidene species. For instance, **2b**,**c**, **3b** and **12b** react with $NaBH_4$ in THF to selectively give the complexes $[Ru_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(R')C(R'')=C(H)N(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2]$ ($R = Bz$, $R' = Me_3Si$, $R'' = H$, **14a**; $R = Me$, $R' = Me_3Si$, $R'' = H$, **14b**; $R = Bz$, $R' = Tol$, $R'' = H$, **15**; $R = Bz$, $R' = R'' = Et$, **16**) (Scheme 7).

The bridging ligand can be described as a μ-vinylalkylidene or, considering also the N(R)(Me) group on C_α, a μ-enaminoalkylidene ligand. Complexes **14**–**16** have been characterised spectroscopically. The IR spectra in CH_2Cl_2 show ν(CO) at 1930–1950 and 1760–1788 cm^{-1} for the terminal and bridging carbonyls, respectively; these bands are ca. 60 cm^{-1} shifted to lower frequencies compared to the starting cationic complexes, in agreement with the neutral character of **14**–**16**. The NMR spectra show the presence in solution of only one isomer for all the complexes studied, as a result of two factors. First, the hydride addition is not only regioselective (α-addition) but also stereoselective;



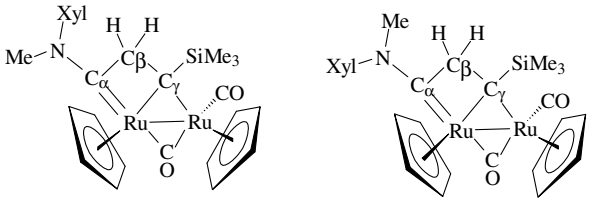
Scheme 7.

in fact the hydride adds *trans* to the $C_\beta(R'')$ substituent. In agreement with this, when $R'' = H$, both $C_\alpha H$ and $C_\beta H$ appear as doublet with $^3J_{HH}$ typical for a *trans* geometry. Second, there is free rotation around the C_α–N bond as a consequence of the lowering of the bond order passing from the starting vinyliminium ligand to the final enaminoalkylidene (vinylalkylidene) ligand. In agreement with this, the two N-bonded methyl groups in **14b** give rise to one single resonance in the ^1H NMR spectrum, whereas they are inequivalent in the parent compound **2c**.

The μ-vinylalkylidene (μ-enaminoalkylidene) ligand shows characteristic resonances in the ^{13}C NMR. When $R'' = H$, C_α, C_β and C_γ resonate at ca. 104, 68 and 160 ppm, respectively; when $R'' = Et$, C_α is high field shifted (96 ppm) whereas C_β and C_γ are down field shifted (94 and 180 ppm, respectively). All the other resonances in the ^1H and ^{13}C spectra are fully in agreement with the proposed structure (see Section 4).

The replacement of the Bz or Me substituents on the iminium group with the bulkier Xyl substituent results in the complete change of the regiochemistry of the reaction. As expected, the Xyl substituent acts as protecting group with respect to the iminium carbon and directs the attack on the adjacent less hindered C_β. Thus, addition of $NaBH_4$ in THF to **2a** and **12a** results in the formation of the bis-alkylidene complexes $[Ru_2\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}C(R')C(H)(R'')CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2]$ ($R' = Me_3Si$, $R'' = H$, **17**; $R' = R'' = Et$, **18**). Compounds **17**–**18** display the usual ν(CO) band pattern consisting in two absorptions attributable to the terminal and bridging CO (e.g., 1918 and 1747 cm^{-1} for **17**). Moreover, a band at ca. 1510 cm^{-1} is present, indicating a partial double bond character of the C_α–N bond, in agreement with the presence of an aminocarbene group in the ligand. The main features of the ^1H NMR spectra are the presence of two distinct resonances for the two inequivalent Cp ligands at 4.9–5.2 ppm, whereas the protons on C_β resonate at 3–4 ppm; when two protons are attached to C_β, a typical geminal $^2J_{HH}$ is observed. In the ^{13}C NMR spectra the bis-alkylidene ligand shows resonances at 250–258 ppm (C_α), 70–84 ppm (C_β) and 130–160 ppm (C_γ). Moreover, the NMR spectra of **17** and **18** show the presence in solution of two isomeric species. In the case of **17**, where two hydrogens are present on C_β, they correspond to the *E* and *Z* forms, due to the different orientations of the Xyl and Me groups on the aminocarbene nitrogen and hindered rotation around the C_α–N bond (Scheme 8), as clearly indicated by the NMR data. The parent complex **2a** was also present in solution as a mixture of the *E* and *Z* forms, in nearly the same proportion (ca. 10:1); this indicates that the hydride addition occurs without altering the relative arrangement of the N-substituents.

The results described show that the reactions of the diruthenium vinyliminium complexes well parallel those of the corresponding diiron compounds. A slight difference consist in the higher tendency, for the diruthenium complexes, to adopt a *trans* geometry for the Cp ligands. Indeed, in the case of **18**, the *cis* and *trans* isomers are observed, both with

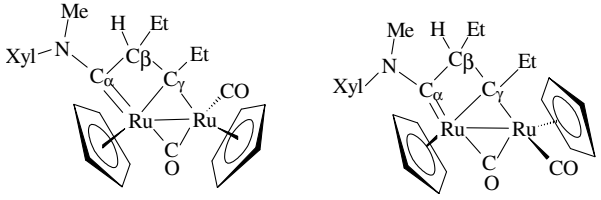


Scheme 8.

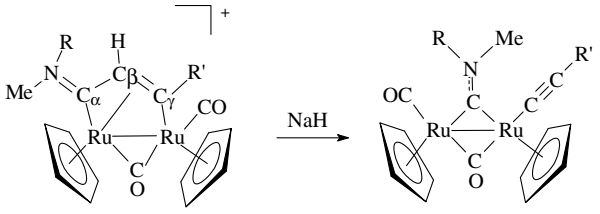
a *Z* configuration of the aminocarbene (Scheme 9). Assignment is based on NMR data which are consistent with the presence of *cis* and *trans* isomers, and by comparison with the structure of the parent complex **12a**, which can exists in both *cis*-*Z* and *trans*-*Z* forms.

2.3. Reactions of the diruthenium vinyliminium complexes with NaH

Bridging vinyliminium complexes derived from the insertion of primary alkynes display a C_β-H hydrogen, which, in the case of the diiron complexes, is slightly acidic and can be removed by treatment with NaH. This reaction has allowed the synthesis of different products (i.e., mono-, di- and tetra-nuclear iron complexes) depending on the nature of the substituents in the parent vinyliminium ligand [5]. By analogy, the deprotonation of the diruthenium complexes **3a**, **2b** and **7a** occurs by treatment of with NaH. The reaction is accompanied by deinsertion of the alkyne, resulting in the formation of $[Ru_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)(C{\equiv}CR')(Cp)_2]$ ($R = Xyl$, $R' = Tol$, **19**; $R = Bz$, $R' = Me_3Si$, **20**; $R = Xyl$, $R' = Me$, **21**), which contain a terminal acetylide and a bridging aminocarbyne ligand (Scheme 10). The IR spectra show terminal and bridging ν(CO) at ca. 1966 and 1795 cm^{-1}, respectively, together with two absorptions at 1515–1547 and 2022–2094 cm^{-1} attributable to $\nu(C{=}N)$ and $\nu(C{\equiv}C)$, respectively. The bridging aminocarbyne carbon resonates in the ^{13}C spectra in the typical low field region (ca. 310 ppm), whereas the two C≡C carbons resonate at 94–112 ppm. Two isomers are present in solution, as usually observed in diruthenium and diiron complexes of the type $[M_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)(L)(Cp)_2]$ (L = acyl, CN, Cl, Br, N_3) [9] with $R \neq Me$. These are due to the different orientation that the substituents R and Me can adopt with respect to the inequivalent M atoms and because of the hindered rotation



Scheme 9.



R	R'		R	R'	
Xyl	Tol	**3a**	Xyl	Tol	**19**
Bz	$SiMe_3$	**2b**	Bz	$SiMe_3$	**20**
Xyl	Me	**7a**	Xyl	Me	**21**

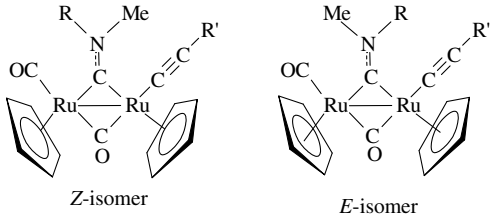
Scheme 10.

around the aminocarbyne C–N bond (*E* and *Z* isomers, Scheme 11). For steric reasons, the *Z* isomer, in which the bulkier Xyl group points far from the acetylide, predominates.

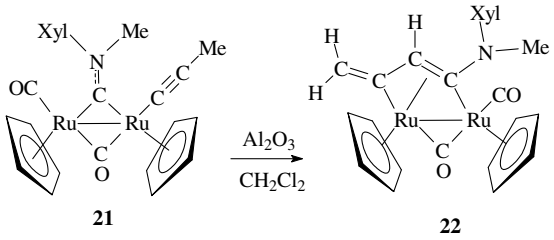
The behaviour of **3a** and **2b** is identical to that of the corresponding diiron counterparts, resulting in the formation of the σ-alkynyl products. By contrast, compound **7a** and its diiron analogue $[Fe_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C(Me)=C(H)C=N(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2]^+$, follow different reaction routes; indeed, treatment of the diiron complex with NaH was reported to give fragmentation of the Fe–Fe bond, yielding the mono-metallic species [Fe(Cp)(CO){CN(Me)(Xyl)-CHC(Me)C(O)}] [5].

Column chromatography on Al_2O_3 of **21**, using CH_2Cl_2 as eluent, results in its isomerisation to give the $\mu\text{-}\eta^1{:}\eta^3$-buta-1,3-diene-1,3-diyl complex $[Ru_2\{\mu\text{-}\eta^3{:}\eta^1\text{-}C[N(Me)(Xyl)]C(H)C=CH_2\}(\mu\text{-}CO)(CO)(Cp)_2]$ (**22**) (Scheme 12). The formation of **22** requires the coupling between the terminal –C≡CMe acetylide ligand and the bridging aminocarbyne followed by 1,3-hydrogen migration.

The molecular structure of **22** (Fig. 3 and Table 3) shows that the molecule maintains the *cis*-$[Ru_2(\mu\text{-}CO)(CO)(Cp)_2]$ core present in the parent compound **21**. The bridging $C[N(Me)(Xyl)]C(H)C=CH_2$ ligand is σ-bonded to Ru(2) [Ru(2)–C(13) 2.108(4) Å] and η^3-coordinated to Ru(1) in an allyl like fashion [Ru(1)–C(13) 2.217(3) Å; Ru(1)–C(14) 2.164(3) Å; Ru(1)–C(15) 2.064(4) Å]. In agreement with this, the C(13)–C(14) [1.424(5) Å] and C(14)–C(15) [1.415(5) Å] distances are almost identical and display a partial π-character. Conversely, C(15)–C(16) [1.317(5) Å] is essentially a double bond and, therefore, the ligand can be considered a 1,2,3-η^3 butadienyl in which one of the substituent on the terminal carbon C(13) has been replaced by a second metal atom, Ru(2). All the bonding parameters



Scheme 11.



Scheme 12.

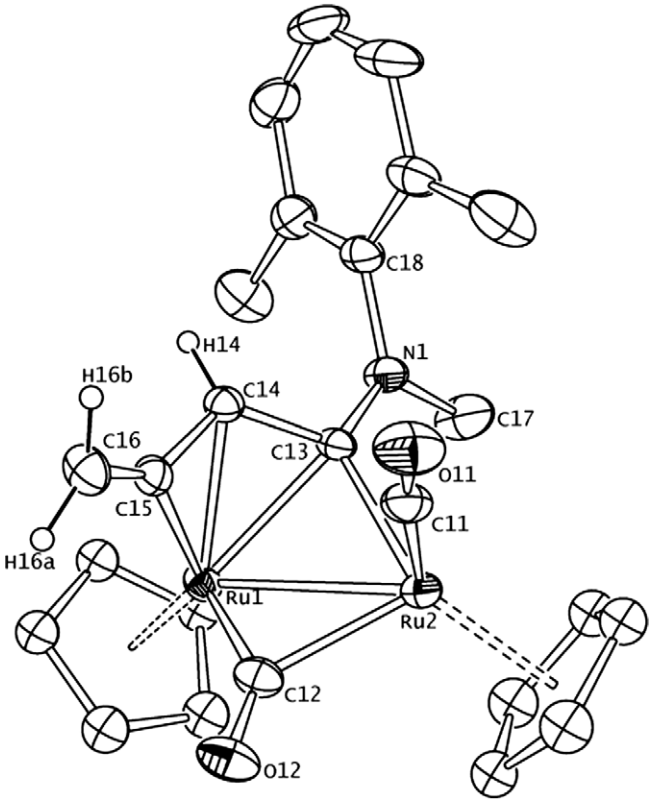
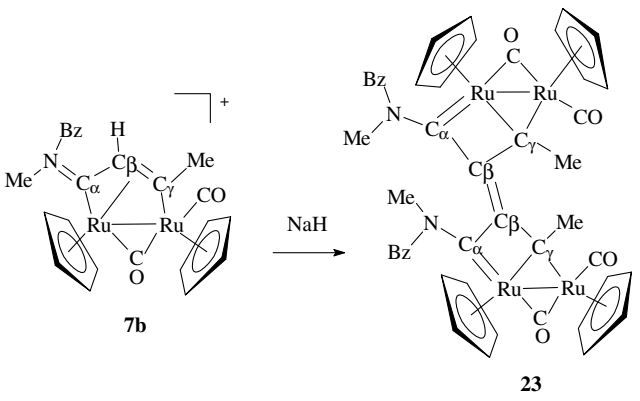


Fig. 3. Molecular structure of **22**, with key atoms labelled (all H atoms, apart from H(14), H(16A) and H(16B), have been omitted). Displacement ellipsoids are at 30% probability level. Only the main image of the disordered Cp ligands bound to Ru(1) and Ru(2) are drawn.

Table 3
Selected bond lengths (Å) and angles (°) for complex **22**

Ru(1)–Ru(2)	2.7251(7)	C(11)–O(11)	1.137(5)
Ru(1)–C(12)	1.962(4)	C(12)–O(12)	1.177(5)
Ru(2)–C(12)	2.076(4)	C(13)–N(1)	1.383(4)
Ru(2)–C(11)	1.853(4)	N(1)–C(17)	1.446(5)
Ru(1)–C(13)	2.217(3)	N(1)–C(18)	1.442(5)
Ru(2)–C(13)	2.108(4)	C(13)–C(14)	1.424(5)
Ru(1)–C(14)	2.164(3)	C(14)–C(15)	1.415(5)
Ru(1)–C(15)	2.064(4)	C(15)–C(16)	1.317(5)
Ru(2)–C(13)–C(14)	119.3(2)	Ru(2)–C(13)–N(1)	124.9(3)
C(13)–C(14)–C(15)	120.6(3)	C(14)–C(13)–N(1)	115.1(3)
C(14)–C(15)–C(16)	141.5(4)	C(13)–N(1)–C(17)	122.9(3)
C(14)–C(15)–Ru(1)	74.3(2)	C(13)–N(1)–C(18)	121.0(3)
C(16)–C(15)–Ru(1)	144.1(3)	C(17)–N(1)–C(18)	116.1(3)



Scheme 13.

relative to the coordination to Ru(1) perfectly resemble the ones previously reported for other 1,2,3-η^3 butadienyl complexes [10]. Finally, the C(13)–N(1) distance [1.383(4) Å] and the almost perfect sp^2 hybridisation of N(1) [sum angle 360.0(5)°] suggest the presence of some π-interaction between the nitrogen and the ligand.

The bridging μ-η^3:η^1-C[N(Me)(Xyl)]C(H)C=CH_2 ligand is characterised by four different resonances in the ^{13}C NMR spectrum at 187.6 (C_γ), 48.7 (C_β), 165.7 (C_α) and 103.4 (=CH_2) ppm; moreover, the ^1H NMR spectrum shows a singlet at 3.72 ppm for $C_\beta H$ and two broad resonances at 5.22 and 4.92 ppm due to the methylidene group =CH_2.

Finally, the reaction of **7b** with NaH results in the formation of the tetranuclear complex [$Ru_2\{\mu$-η^1:η^2-C(Me)CCN(Me)(Bz)$\}(\mu$-CO)(CO)$(Cp)_2]_2$ (**23**) in moderate yields (56%) (Scheme 13). Again, the reaction parallels that described for the diiron counterpart and the spectroscopic properties of **23** closely resemble those of the corresponding tetra-iron species [$Fe_2\{\mu$-η^1:η^2-C(Me)CCN$(Me)_2\}(\mu$-CO)(CO)$(Cp)_2]_2$ [5]. The mechanism of this intriguing dimerisation reaction remains unclear: one possibility is that C_β-H proton removal is accompanied by a change in the bridging ligand, which might assume the bis-alkylidene coordination mode. This would generate an uncoordinated C_β carbon, displaying carbene character, which should dimerise. Similar dimerisations have been reported for the deprotonated forms of some alkoxy- and amino-carbene complexes, which undergo oxidative coupling to give bridging bis-carbene complexes in an overall sequence described as "dehydrodimerisation" [11].

3. Conclusions

The data reported in this paper demonstrate the possibility of extending the preparation of bridging vinyliminium ligands, previously reported for diiron complexes, to diruthenium compounds. Thus, alkyne insertion into the metal carbyne bond is of general character and is not influenced by the nature of the metal (Fe or Ru). Moreover, our studies show a near complete analogy between the two cases, regarding both the reactivity and stereochemistry of the products. These results are not obvious because related complexes, containing the $M_2(CO)_2(Cp)_2$ frame, show distinct behaviours for iron and ruthenium. As an example the diiron bridging methylidyne complex [$Fe_2(\mu$-CH)-$(\mu$-CO)$(CO)_2(Cp)_2]^+$ investigated by Casey, has not a ruthenium counterpart [12]. Likewise, the large variety of reactions described by Knox on diruthenium complexes [6,13] has been only limitedly reproduced by the corresponding iron complexes [14]. On the other hand, diiron and diruthenium bridging amino carbyne complexes [$M_2\{\mu$-CN(R)(Me)$\}(\mu$-CO)$(CO)_2(Cp)_2]^+$ have shown a very similar reactivity towards the addition of nucleophiles [15].

Our findings on the chemistry of the diruthenium vinyliminium complexes, together with those previously reported on the diiron compounds [4,5], evidence the electrophilic character of the vinyliminium ligand.

The addition of hydride on the vinyliminium ligand is of general character and is influenced by the steric demand and electronic properties of the substituents at the iminium nitrogen rather than by the nature of the metal atoms.

However, some differences have been found, like the higher presence of *trans* isomers in the diruthenium complexes. In addition, fragmentation of the M–M bond, was observed for some of the diiron vinyliminum complexes, but not in the corresponding diruthenium species. This suggests a greater stability for the diruthenium complexes, but is not be considered a conclusive evidence because of the limited number of compounds examined so far.

4. Experimental details

4.1. General

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 on 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 on a Waters Micromass ZQ 4000 with samples dissolved in CH_3CN. All NMR measurements were performed on Varian Gemini 300, Varian Mercury Plus 400 and Varian Inova 600 instruments. The chemical shifts for ^1H and ^{13}C were referenced to internal TMS. The spectra were fully assigned via DEPT experiments and ^1H,^{13}C correlation measured using gs-HSQC and gs-HMBC experiments [16]; ^1H,^1H correlations were determined by gs-COSY experiments [17]. When two isomers were present, 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. Monodimensional NOE measurements were recorded using the DPFGSE-NOE sequence [7], whereas bidimensional measurements were recorded using a NOESY sequence modified with homospoil gradients [8]. All chemicals were used as received from Aldrich Co., except [$Ru_2\{\mu$-CN(Me)(R)$\}(\mu$-

$CO)(CO)_2(Cp)_2][SO_3CF_3]$ (R = Xyl, Bz, Me) [14a] and $[Ru_2\{\mu\text{-}CN(Me)_2\}(\mu\text{-}CO)(CO)(MeCN)(Cp)_2][SO_3CF_3]$, **1c** [9b], which were prepared by published methods.

4.2. Synthesis of *[Ru$_2${μ-CN(Me)(R)}(μ-CO)(CO)-(MeCN)(Cp)$_2$][SO$_3$CF$_3$] (R = Xyl, **1a**; Bz, **1b**)*

Me_3NO (44.0 mg, 0.587 mmol) was added to a solution of $[Ru_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)_2(Cp)_2][SO_3CF_3]$ (0.351 mmol) in CH_3CN (10 mL). After stirring at room temperature for 1 h, the solvent was removed in vacuo and the residue washed with petroleum ether (2 × 5 mL), dissolved in CH_2Cl_2 (5 mL) and filtered through a celite pad. Removal of the solvent under reduced pressure from the filtrated afforded the final product as a yellow-orange powder.

1a: Yield: 208.8 mg (82%). Anal. Calc. for $C_{25}H_{25}F_3N_2O_5Ru_2S$: C, 41.43; H, 3.48; N, 3.87. Found: C, 41.12; H, 3.55; N, 3.69. IR (CH_2Cl_2, 293 K): *ν* (cm^{-1}) 1982vs, 1820s (CO), 1530m (C═N). ^1H NMR (CD_2Cl_2, 293 K) Isomer α: *δ* 7.31–7.21 (m, 3H, arom), 5.35, 4.94 (s, 10H, Cp), 4.28 (s, 3H, N*Me*), 2.39, 2.19 (s, 6H, $C_6H_3Me_2$), 2.21 (s, 3H, *Me*CN); Isomer β: *δ* 7.31–7.21 (m, 3H, arom), 5.52, 4.71 (s, 10H, Cp), 4.18 (s, 3H, N*Me*), 2.29, 2.16 (s, 6H, $C_6H_3Me_2$), 2.15 (s, 3H, *Me*CN). α/β = 8.5. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 293 K) Isomer α: *δ* 310.8 (μ-*C*), 235.2 (μ-*C*O), 200.1 (*C*O), 147.8 (*C*-ipso Xyl), 132.7, 132.0 (*C*-Me Xyl), 129.7, 128.8, 128.6 (*C*H Xyl), 118.7 (*C*≡N), 89.6, 88.1 (Cp), 53.3 (N-*Me*), 18.3, 17.2 ($C_6H_3Me_2$), 3.7 (*Me*CN); Isomer β: *δ* 310.6 (μ-*C*), 236.1 (μ-*C*O), 199.8 (*C*O), 147.7 (C-ipso Xyl), 132.8, 132.1 (*C*-Me Xyl), 129.7, 128.9, 128.7 (*C*H Xyl), 90.5, 87.4 (Cp), 54.6 (N-*Me*), 18.5, 17.3 ($C_6H_3Me_2$), 3.8 (*Me*CN).

1b: Yield: 227.0 mg (91%). Anal. Calc. for $C_{24}H_{23}F_3N_2O_5Ru_2S$: C, 40.56; H, 3.26; N, 3.94. Found: C, 40.89; H, 3.04; N, 373. IR (CH_2Cl_2, 293 K): *ν* (cm^{-1}) 1982vs, 1817s (CO), 1588w, 1574m, 1550m (C═N). ^1H NMR (CD_2Cl_2, 293 K) Isomer α: *δ* 7.50–7.20 (m, 5H, arom), 5.56 (s, 2H, C*H*$_2$Ph), 5.40, 5.29 (s, 10H, Cp), 3.94 (s, 3H, N*Me*), 2.16 (s, 3H, *Me*CN); Isomer β: *δ* 7.50–7.20 (m, 5H, arom), 5.77 (s, 2H, C*H*$_2$Ph), 5.56, 5.21 (s, 10H, Cp), 3.89 (s, 3H, N*Me*), 2.06 (s, 3H, *Me*CN). α/β = 1.5.

4.3. Synthesis of *[Ru$_2${μ-η^1:η^3-C(R′)═CHC═N(Me)(R)}-(μ-CO)(CO)(Cp)$_2$][SO$_3$CF$_3$] (R = Xyl, R′ = Me$_3$Si, **2a**; R = Bz, R′ = Me$_3$Si, **2b**; R = Me, R′ = Me$_3$Si, **2c**; R = Xyl, R′ = Tol, **3a**; R = Bz, R′ = Tol, **3b**)*

A solution of **1a**–**c** (0.100 mmol) and the appropriate alkyne R′C≡CH (0.300 mmol; R′ = Me_3Si, Tol) in THF (12 mL) was refluxed for 1 h affording an orange solution. Hence, the solvent was removed under reduced pressure and the residue dissolved in CH_2Cl_2 (5 mL) and chromatographed through a Al_2O_3 column. The final product was obtained as an orange fraction using CH_3CN as eluent.

2a: Yield: 56.3 mg (72%). Anal. Calc. for $C_{28}H_{32}F_3NO_5Ru_2SSi$: C, 43.01; H, 4.13; N, 1.79. Found: C, 42.89; H, 4.26; N, 1.68. IR (CH_2Cl_2, 293 K): *ν* (cm^{-1}) 2000vs, 1823s (CO), 1628ms (C═N). ^1H NMR ($CDCl_3$, 293 K) Isomer *E*: *δ* 7.24–6.93 (m, 3H, *Xyl*), 5.69, 5.53 (s, 10H, *Cp*), 5.02 (s, 1H, Cβ-*H*), 4.00 (s, 3H, N-*Me*), 2.18, 1.92 (s, 3H, $Me_2C_6H_3$), 0.29 (s, 1H, Me_3Si); Isomer *Z*: *δ* 7.24–6.93 (m, 3H, *Xyl*), 5.96 (s, 1H, Cβ-*H*), 5.59, 5.42 (s, 10H, *Cp*), 3.67 (s, 3H, N-*Me*), 2.41, 2.03 (s, 3H, $Me_2C_6H_3$), 0.45 (s, 1H, Me_3Si). Isomer ratio *E*/*Z* = 10. ^{13}C NMR ($CDCl_3$, 293 K) Isomer *E*: *δ* 231.5 (μ-*C*O), 221.1 (C_α-N), 197.6 (*C*O), 188.1 (C_γ), 144.3 (*C*-ipso Xyl), 132.0, 131.5 (*C*-Me Xyl), 129.7, 129.5, 129.4 (*C*H Xyl), 91.3, 88.7 (*Cp*), 63.1 (C_β), 47.4 (N-*Me*), 17.9, 17.8 ($Me_2C_6H_3$), 2.2 (Me_3Si); Isomer *Z*: *δ* 231.5 (μ-*C*O), 220.7 (C_α-N), 197.4 (*C*O), 188.0 (C_γ), 144.1–128.3 (arom), 90.0, 88.2 (*Cp*), 63.4 (C_β), 50.9 (N-*Me*), 19.6, 19.3 ($Me_2C_6H_3$), 2.5 (Me_3Si).

2b: Yield: 61.4 mg (80%). Anal. Calc. for $C_{27}H_{30}F_3NO_5Ru_2SSi$: C, 42.24; H. 3.94, N, 1.82. Found: C, 41.98; H, 4.05, N, 1.76. IR (CH_2Cl_2, 293 K): *ν* (cm^{-1}) 1988vs, 1818s (CO), 1669ms (C═N). ^1H NMR ($CDCl_3$, 293 K) Isomer *E*: *δ* 7.50–7.20 (m, 5H, *Ph*), 5.61, 5.40 (s, 10H, *Cp*), 4.93 (s, 1H, Cβ-*H*), 4.84, 4.71 (d AB, $^2J_{HH}$ = 14 Hz, 2H, C*H*$_2$Ph), 3.62 (s, 3H, N-*Me*), 0.34 (s, 9H, SiMe_3); Isomer *Z*: *δ* 7.50–7.20 (m, 5H, *Ph*), 5.64, 5.42 (s, 10H, *Cp*), 5.70, 5.26 (d, $^2J_{HH}$ = 7 Hz, 2H, C*H*$_2$Ph), 5.19 (s, 1H, Cβ-*H*), 3.21 (s, 3H, N-*Me*), 0.44 (s, 9H, SiMe_3). Isomer ratio *E*/*Z* = 1.1. ^{13}C NMR ($CDCl_3$, 293 K) Isomer *E*: *δ* 230.4 (μ-*C*O), 216.7 (C_α-N), 198.1 (*C*O), 184.8 (C_γ), 127.5–132.5 (arom), 88.4, 90.9 (*Cp*), 66.6 (*C*H$_2$Ph), 62.8 (C_β), 44.4 (N-*Me*), 2.5 (SiMe_3); Isomer *Z*: *δ* 230.4 (μ-*C*O), 216.1 (C_α-N), 197.6 (*C*O), 183.4 (C_γ), 127.5–132.5 (*Ph*), 84.4, 90.9 (*Cp*), 66.6 (*C*H$_2$Ph), 62.2 (C_β), 47.4 (N-*Me*), 2.3 (SiMe_3).

2c: Yield: 53.3 mg (77%). Anal. Calc. for $C_{21}H_{26}F_3NO_5Ru_2SSi$: C, 36.46; H. 3.79, N, 2.02. Found: C, 36.81; H, 3.50, N, 2.26. IR (CH_2Cl_2, 293 K): *ν* (cm^{-1}) 1988vs, 1815s (CO), 1682ms (C═N). ^1H NMR ($CDCl_3$, 293 K): *δ* 5.53, 5.32 (s, 10H, *Cp*), 5.42 (s, 1H, Cβ-*H*), 3.63, 3.36 (s, 3H, N-*Me*), 0.34 (s, 1H, Me_3Si). ^{13}C NMR ($CDCl_3$, 293 K): *δ* 230.2 (μ-*C*O), 216.5 (C_α-N), 197.6 (*C*O), 183.1 (C_γ), 90.7, 88.1 (*Cp*), 62.2 (C_β), 50.4, 45.7 (N-*Me*), 2.3 (Me_3Si).

3a: Yield: 60.0 mg (75%). Anal. Calc. for $C_{32}H_{30}F_3NO_5Ru_2S$: C, 48.01; H. 3.78, N, 1.75. Found: C, 47.87; H, 3.92, N, 1.63. IR (CH_2Cl_2, 293 K): *ν* (cm^{-1}) 2002vs, 1827s (CO), 1629ms (C═N). ^1H NMR ($CDCl_3$, 293 K) Isomer *E*: *δ* 7.37–7.03 (m, 7H, *arom*), 5.68, 5.42 (s, 10H, *Cp*), 4.67 (s, 1H, Cβ-*H*), 4.01 (s, 3H, N-*Me*), 2.36, 2.15, 1.97 (s, 9H, *p*-MeC_6H_4 + $Me_2C_6H_3$); Isomer *Z*: *δ* 7.37–7.03 (m, 7H, *arom*), 5.41, 5.18 (s, 10H, *Cp*), 5.09 (s, 1H, Cβ-*H*), 3.70 (s, 3H, N-*Me*), 2.38, 2.31, 2.07 (s, 9H, *p*-MeC_6H_4 + $Me_2C_6H_3$). Isomer ratio *E*/*Z* = 5. ^{13}C NMR ($CDCl_3$, 293 K) Isomer *E*: *δ* 228.0 (μ-*C*O), 220.8 (C_α-N), 197.6 (*C*O), 190.9 (C_γ), 151.5–126.6 (arom), 93.6, 89.3 (*Cp*), 62.0 (C_β), 47.1 (N-*Me*), 21.0 (*p*-MeC_6H_4), 17.9, 17.5 ($Me_2C_6H_3$); Isomer *Z*: *δ* 228.3 (μ-*C*O), 221.1 (C_α-N), 198.2 (*C*O), 189.8 (C_γ), 151.5–126.6 (arom), 93.8, 89.3 (*Cp*), 62.0 (C_β), 50.8 (N-*Me*), 21.1 (*p*-MeC_6H_4), 18.0, 17.6 ($Me_2C_6H_3$).

3b: Yield: 58.9 mg (75%). Anal. Calc. for $C_{31}H_{28}F_3NO_5Ru_2S$: C, 47.39; H, 3.59, N, 1.78. Found: C, 46.97; H, 3.44, N, 1.67. IR (CH_2Cl_2, 293 K): ν (cm^{-1}) 1990vs, 1820s (CO), 1666ms (C=N). ^1H NMR ($CDCl_3$, 293 K) Isomer *E*: δ 7.42–7.11 (m, 9H, *Ph + Tol*), 5.50, 5.31 (s, 10H, *Cp*), 4.94 (s, 1H, C_β-*H*), 4.86, 4.72 (d AB, $^2J_{HH} = 14.2$ Hz, 2H, CH_2Ph), 3.62 (s, 3H, N-*Me*), 2.37 (s, 3H, *p*-*Me*C_6H_4); Isomer *Z*: δ 7.42–7.11 (m, 9H, *Ph + Tol*), 5.52, 5.34 (s, 10H, *Cp*), 5.29 (s, 1H, C_β-*H*), 5.24 (d, $^2J_{HH} = 14.1$ Hz, 1H, CH_2Ph. Second doublet hidden by Cp), 3.22 (s, 3H, N-*Me*), 2.38 (s, 3H, *p*-*Me*C_6H_4). Isomer ratio *E*/*Z* = 1.3. ^{13}C NMR ($CDCl_3$, 293 K) Isomer *E*: δ 230.0 (μ-*C*O), 216.3 (C_α-N), 197.8 (*C*O), 187.2 (C_γ), 151.5, 137.0 (*C*-ipso Ph + Tol), 132.0 (*C*-Me Tol), 129.8–128.8 (*C*H Ph + Tol), 127.2 (*p*-*C*H Ph), 93.2, 89.2 (*Cp*), 66.7 (*C*H_2Ph), 59.8 (C_β), 44.3 (N-*Me*), 21.0 (*p*-*Me*C_6H_4); Isomer *Z*: δ 231.6 (μ-*C*O), 216.5 (C_α-N), 197.5 (*C*O), 188.3 (C_γ), 151.5, 137.0 (*C*-ipso Ph + Tol), 131.4 (*C*-Me Tol), 129.8–128.8 (*C*H Ph + Tol), 127.3 (*p*-*C*H Ph), 93.2, 89.3 (*Cp*), 62.8 (*C*H_2Ph), 60.0 (C_β), 47.2 (N-*Me*), 21.0 (*p*-*Me*C_6H_4).

4.4. Synthesis of [Ru_2{μ-η^1:η^3-C(R′)=CHC=N(Me)-(R)}(μ-CO)(CO)(Cp)$_2$][SO_3CF_3] (R = Bz, R′ = CH_2OH, **4**; R = Bz, R′ = CO_2Me, **5a**; R = Me, R′ = CO_2Me, **5b**)

A solution of **1** (0.100 mmol) and the appropriate alkyne R′C≡CH (0.300 mmol; R′ = CH_2OH, CO_2Me) in THF (12 mL) was refluxed for 1 h affording an orange-red solution. After removal of the solvent in vacuo, the residue was washed with petroleum ether (3 × 5 mL) and Et_2O (3 × 5 mL), dissolved in CH_2Cl_2 (5 mL), filtered through celite and dried in vacuo affording the final product as an orange-red powder.

4: Yield: 54.4 mg (75%). Anal. Calc. for $C_{25}H_{24}F_3NO_6Ru_2S$: C, 41.37; H, 3.33, N, 1.93. Found: C, 41.56; H, 3.12, N, 2.09. IR (CH_2Cl_2, 293 K): ν (cm^{-1}) 1989vs, 1816s (CO), 1667ms (C=N). ^1H NMR ($CDCl_3$, 293 K) Isomer *Z*: δ 7.39–7.13 (m, 5H, *Ph*), 5.97 (s, 1H, C_β-*H*), 5.62, 5.46 (m, 2H, CH_2OH), 5.59, 5.35 (s, 10H, *Cp*), 5.14, 5.03 (d AB, $^2J_{HH} = 13.9$ Hz, 2H, CH_2Ph), 3.16 (s, 3H, N-*Me*), 0.85 (br, 1H, O*H*); Isomer *E*: δ 7.39–7.13 (m, 5H, *Ph*), 6.00 (s, 1H, C_β-*H*), 5.64, 5.42 (m, 2H, CH_2OH), 5.59, 5.37 (s, 10H, *Cp*), 4.85, 4.44 (d, $^2J_{HH} = 14.3$ Hz, 2H, CH_2Ph), 3.42 (s, 3H, N-*Me*), 0.85 (br, 1H, O*H*); Isomer ratio *Z*/*E* = 1.2. ^{13}C NMR ($CDCl_3$, 293 K) Isomer *Z*: δ 231.7 (μ-*C*O), 218.0 (C_α-N), 197.3 (*C*O), 191.6 (C_γ), 131.9 (*C*-ipso Ph), 129.3–128.4 (*C*H arom), 91.0, 88.6 (*Cp*), 74.8 (*C*H_2OH), 62.8 (*C*H_2Ph), 53.8 (C_β), 47.1 (N-*Me*); Isomer *E*: δ 230.6 (μ-*C*O), 218.4 (C_α-N), 197.5 (*C*O), 191.5 (C_γ), 131.5 (*C*-ipso Ph), 129.3–128.4 (*C*H arom), 91.0, 88.6 (*Cp*), 74.8 (*C*H_2OH), 67.8 (*C*H_2Ph), 53.6 (C_β), 43.1 (N-*Me*). ESI MS: ES+ *m*/*z* 578.

5a: Yield: 57.3 mg (76%). Anal. Calc. for $C_{26}H_{24}F_3NO_7Ru_2S$: C, 41.44; H, 3.21, N, 1.86. Found: C, 41.17; H, 3.34, N, 1.92. IR (CH_2Cl_2, 293 K): ν (cm^{-1}) 1997vs, 1827s (CO), 1728s, 1714sh (CO_2Me), 1671ms (C=N). ^1H NMR ($CDCl_3$, 293 K) Isomer *Z*: δ 7.39–7.18 (m, 5H, *Ph*), 5.79 (s, 1H, C_β-*H*), 5.56, 5.48 (s, 10H, *Cp*), 5.22, 5.18 (d AB, $^2J_{HH} = 15.4$ Hz, 2H, CH_2Ph), 3.94 (s, 3H, CO_2Me), 3.21 (s, 3H, N-*Me*); Isomer *E*: δ 7.39–7.18 (m, 5H, *Ph*), 5.61 (s, 1H, C_β-*H*), 5.54, 5.47 (s, 10H, *Cp*), 4.91, 4.65 (d, $^2J_{HH} = 14.0$ Hz, 2H, CH_2Ph), 3.98, (s, 3H, +CO_2Me), 3.52 (s, 3H, N-*Me*). Isomer ratio *Z*/*E* = 1.7. ^{13}C NMR ($CDCl_3$, 293 K) Isomer *Z*: δ 228.7 (μ-*C*O), 214.4 (C_α-N), 196.3 (*C*O), 175.6 (C_γ), 165.9 (*C*O_2Me), 134.4–122.7 (*C*H Ph), 92.0, 89.7 (*Cp*), 63.0 (*C*H_2Ph), 58.8 (C_β), 52.9 (CO_2Me), 45.1 (N*Me*); Isomer *E*: δ 227.2 (μ-*C*O), 214.4 (C_α-N), 196.6 (*C*O), 175.6 (C_γ), 165.2 (*C*O_2Me), 134.4–122.7 (*C*H Ph), 92.0, 89.7 (*Cp*), 67.4 (*C*H_2Ph), 58.5 (C_β), 52.5 (CO_2Me), 43.7 (N*Me*).

5b: Yield: 57.6 mg (85%). Anal. Calc. for $C_{20}H_{20}F_3NO_7Ru_2S$: C, 35.45; H, 2.98, N, 2.07. Found: C, 35.16; H, 3.12, N, 2.29. IR (CH_2Cl_2, 293 K): ν (cm^{-1}) 1996vs, 1828s (CO), 1735s (CO_2Me). ^1H NMR ($CDCl_3$, 293 K): δ 5.49 (s, 1H, C_β-*H*), 5.41, 5.34 (s, 10H, *Cp*), 3.83 (s, 3H, CO_2Me), 3.53, 3.30 (s, 6H, NMe_2). ^{13}C NMR ($CDCl_3$, 293 K): δ 227.8 (μ-*C*O), 214.6 (C_α-N), 196.7 (*C*O), 175.8 (C_γ), 167.7 (*C*O_2Me), 92.1, 89.8 (*Cp*), 58.7 (C_β), 53.1 (CO_2Me), 50.8, 46.2 (NMe_2).

4.5. Synthesis of [Ru_2{μ-η^1:η^3-C[$(CH_2)_4$CCH]=CHC=N(Me)(Xyl)}(μ-CO)(CO)(Cp)$_2$][SO_3CF_3] (**6**)

A solution of **1a** (88.1 mg, 0.121 mmol) and HC≡C$(CH_2)_4$C≡CH (02 mL, 1.35 mmol) in THF (1 mL) was refluxed for 1 h affording an orange solution. Hence, the solvent was removed under reduced pressure and the residue dissolved in CH_2Cl_2 (5 mL) and chromatographed through a Al_2O_3 column. The final product was obtained as an orange fraction using CH_3CN as eluent. Yield: 71.7 mg (75%). Anal. Calc. for $C_{31}H_{32}F_3NO_5Ru_2S$: C, 47.14; H, 4.08, N, 1.77. Found: C, 47.49; H, 3.74, N, 1.95. IR (CH_2Cl_2, 293 K): ν (cm^{-1}) 2118w (C≡C), 2000vs, 1823s (CO), 1631m, 1588w (C=N). ^1H NMR ($CDCl_3$, 293 K) Isomer *E*: δ 7.33–6.95 (m, 3H, *arom*), 5.66, 5.48 (s, 10H, *Cp*), 4.64 (s, 1H, C_β-*H*), 3.90 (s, 3H, N-*Me*), 3.64, 3.27 (m, 2H, C(1)H_2), 2.34 (m, 2H, C(3)H_2), 2.17, 1.87 (s, 6H, *Me*$_2$$C_6H_3$), 1.92 (t $^4J_{HH} = 2.7$ Hz, 1H, C≡C*H*), 1.90, 1.57 (m, 2H, C(2)H_2), 1.4–1.7 (m, 2H, C(4)H_2); Isomer *Z*: δ 7.40–7.10 (m, 3H, *arom*), 5.74 (s, 1H, C_β-*H*), 5.62, 5.08 (s, 10H, *Cp*), 3.61 (s, 3H, N-*Me*), 3.70, 3.60 (m, 2H, C(1)H_2), 2.40, 2.03 (s, 6H, *Me*$_2$$C_6H_3$), 2.30 (m, 2H, C(3)$H_2$), 2.10, 1.90 (m, 2H, C(2)H_2), 2.03 (t, $^4J_{HH} = 2.6$ Hz, 1H, C≡C*H*), 1.50 (m, 2H, C(4)H_2); Isomer ratio *E*/*Z* = 10. ^{13}C NMR ($CDCl_3$, 293 K) Isomer *E*: δ 229.5 (μ-*C*O), 222.4 (C_α-N), 197.8 (*C*O), 196.6 (C_γ), 144.1 (*C*-ipso Xyl), 132.0, 131.2 (*C*-Me Xyl), 129.8–128.8 (*C*H Xyl), 92.2, 88.9 (*Cp*), 84.2 (*C*≡CH), 69.0 (C≡*C*H), 59.4 (C_β), 55.1 (*C*(1)H_2), 47.0 (N-*Me*), 34.4 (*C*(2)H_2), 27.8 (*C*(4)H_2), 18.2 (*C*(3)H_2), 17.9, 17.4 (*Me*$_2$$C_6H_3$); Isomer *Z*: δ 228.7 (μ-*C*O), 221.7 (C_α-N), 198.6 (*C*O), 195.9 (C_γ), 141.4 (*C*-ipso Xyl), 134.3, 133.2 (*C*-Me Xyl), 129.7, 129.5, 128.8 (*C*H Xyl), 92.2, 92.1 (*Cp*), 84.6 (*C*≡CH), 68.8 (C≡*C*H), 60.2 (C_β), 54.5

($C(1)H_2$), 50.7 (N-*Me*), 34.4 ($C(2)H_2$), 27.8 ($C(4)H_2$), 18.2 ($C(3)H_2$), 17.9, 17.7 ($Me_2C_6H_3$). ESI MS: ES+ *m*/*z* 642.

4.6. Synthesis of [$Ru_2\{\mu$-η^1:η^3-C(Me)=CHC=N(Me)-(R)$\}(\mu$-CO)(CO)$(Cp)_2][SO_3CF_3]$ (R = Xyl, **7a**; Bz, **7b**; Me, **7c**)

A solution of **1** (0.304 mmol) in CH_2Cl_2 (15 mL) was saturated with MeC≡CH and stirred overnight at room temperature. Hence, the resulting solution was chromatographed through a Al_2O_3 column. The final product was obtained as a yellow-orange fraction using MeOH as eluent.

7a: Yield: 169.4 mg (77%). Anal. Calc. for $C_{26}H_{26}F_3NO_5Ru_2S$: C, 43.15; H, 3.62, N, 1.94. Found: C, 42.98; H, 3.86, N, 2.08. IR (CH_2Cl_2, 293 K): *v* (cm^{-1}) 1998vs, 1824s (CO), 1628ms (C=N). ^{1}H NMR ($CDCl_3$, 293 K): δ 7.07–6.87 (m, 3H, *arom*), 5.60, 5.39 (s, 10H, *Cp*), 4.57 (s, 1H, C_β-*H*), 3.82 (s, 3H, N-*Me*), 3.32 (s, 3H, C_γ-*Me*), 2.10, 1.79 (s, 6H, $Me_2C_6H_3$). ^{13}C NMR ($CDCl_3$, 293 K): δ 229.4 (μ-*C*O), 222.5 (C_α-N), 198.0 (*C*O), 190.7 (C_γ), 144.3 (*C*-ipso Xyl), 132.2, 131.4 (*C*-Me Xyl), 129.8, 129.5 (*C*H Xyl), 92.6, 89.0 (*Cp*), 60.8 (C_β), 47.2 (N-*Me*), 43.2 (C_γ-*Me*), 18.7, 17.6 ($Me_2C_6H_3$).

7b: Yield: 175.0 mg (81%). Anal. Calc. for $C_{25}H_{25}F_3NO_5Ru_2S$: C, 42.25; H, 3.55, N, 1.97. Found: C, 42.61; H, 3.74, N, 1.48. IR (CH_2Cl_2, 293 K): *v* (cm^{-1}): 1988vs (CO), 1817s (μ-CO), 1666mw, 1606m (C=N). ^{1}H NMR ($CDCl_3$, 293 K): Isomer *E*: δ 7.33–7.09 (m, 5H, *Ph*), 5.28, 4.42 (d, $^2J_{HH} = 14.3$ Hz, 2H, C*H*$_2$Ph), 5.53, 5.27 (s, 10H, *Cp*), 5.22 (s, 1H, C_β-*H*), 3.41 (s, 3H, C_γ-*Me*), 3.36 (s, 3H, N-*Me*); Isomer *Z*: δ 7.33–7.09 (m, 5H, *Ph*), 5.84, 4.71 (d, $^2J_{HH} = 14.6$ Hz, 2H, C*H*$_2$Ph), 5.54, 5.26 (s, 10H, *Cp*), 5.12 (s, 1H, C_β-*H*), 3.43 (s, 3H, C_γ-*Me*), 3.04 (s, 3H, N-*Me*). Isomer ratio *E*/*Z* = 1.2. ^{13}C NMR ($CDCl_3$, 293 K) Isomer *E*:δ 230.9 (μ-*C*O), 217.9 (C_α-N), 198.2 (*C*O), 187.6 (C_γ), 131.8 (*C*-ipso Ph), 129.5–127.4 (*C*H Ph), 92.3, 88.9 (*Cp*), 67.7 (*C*H$_2$Ph), 59.3 (C_β), 43.5 (N-*Me*), 42.3 (C_γ-*Me*); Isomer *Z*: δ 232.3 (μ-*C*O), 218.1 (C_α-N), 197.9 (*C*O), 187.9 (C_γ), 132.3 (*C*-ipso Ph), 129.5–127.4 (*C*H Ph), 92.3, 89.0 (*Cp*), 67.6 (*C*H$_2$Ph), 59.6 (C_β), 47.2 (N*Me*), 42.4 (C_γ-*Me*).

7c: Yield: 169.5 mg (88%). Anal. Calc. for $C_{19}H_{20}F_3NO_5Ru_2S$: C, 36.02; H, 3.18, N, 2.21. Found: C, 35.87; H, 3.49, N, 2.05. IR (in CH_2Cl_2, 293 K) *v* (cm^{-1}): 1987vs (CO), 1817s (μ-CO), 1680ms (C=N). ^{1}H NMR ($CDCl_3$, 298 K): δ 5.49, 5.26 (s, 10H, *Cp*), 5.08 (s, 1H, C_β-*H*), 3.52, 3.27 (s, 6H, NMe_2), 3.40 (s, 3H, C_γ-*Me*), ^{13}C NMR ($CDCl_3$, 298 K): δ 231.3 (μ-*C*O), 217.4 (C_α-N), 197.9 (*C*O), 186.6 (C_γ), 92.1, 88.8 (*Cp*), 59.2 (C_β), 50.4, 46.0 (NMe_2), 42.2 (C_γ-*Me*).

4.7. Synthesis of [$Ru_2\{\mu$-CN(Me)(Xyl)$\}(\mu$-CO)(CO)-(Cl)$(Cp)_2$] (**8**)

A solution containing **1a** (58.1 mg, 0.080 mmol) and (Et_4N)(Cl) (90.2 mg, 0.532 mmol) in THF (10 mL) was refluxed for 1 h. Then, the solvent was removed under reduced pressure and the residue dissolved in CH_2Cl_2 and chromatographed through Al_2O_3; the product was obtained as an orange fraction using THF as eluent. Yield: 34.7 mg (76%). Anal. Calc. for $C_{22}H_{22}ClNORu_2$: C, 46.36; H, 3.89; N, 2.46. Found: C, 46.58; H, 3.72; N, 2.38. IR (CH_2Cl_2, 293 K): *v* (cm^{-1}) 1970vs, 1797s (CO), 1509ms (C=N). ^{1}H NMR (CD_2Cl_2, 293 K): δ 7.24–7.16 (m, 3H, arom), 5.16, 4.81 (s, 10H, Cp), 4.28 (s, 3H, N*Me*), 2.29, 2.14 (s, 6H, $C_6H_3Me_2$).

4.8. Synthesis of [$Ru_2\{\mu$-η^1:η^3C(C(Me)=CH_2)=CHC=N(Me)(Xyl)$\}(\mu$-CO)(CO)$(Cp)_2$] [SO_3CF_3] (**9**)

$AgSO_3CF_3$ (25.0 mg, 0.097 mmol) was added to a solution containing **8** (34.1 mg, 0.060 mmol) and HC≡CC(Me)=CH_2 (0.4 mL, 4.21 mmol) in CH_2Cl_2 (5 mL) at −50 °C. After stirring at room temperature for 1 h, the mixture was filtered through Al_2O_3 using CH_3CN in order to remove AgCl. Hence, 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 a bright orange fraction using CH_3CN as eluent. Yield: 31.4 mg (71%). Anal. Calc. for $C_{27}H_{28}F_3NO_5Ru_2S$: C, 43.96; H, 3.83, N, 1.90. Found: C, 44.03; H, 3.77, N, 1.99. IR (CH_2Cl_2, 293 K): *v* (cm^{-1}) 2002vs, 1828s (CO), 1627ms, 1588w (C=N). ^{1}H NMR ($CDCl_3$, 293 K) Isomer *Z*: δ 7.36–6.95 (m, 3H, *Xyl*), 5.47, 5.10 (s, 10H, *Cp*), 5.02 (br, 1H, C_β-*H*), 4.85 (br, 2H, C*H*$_2$=), 3.61 (s, 3H, N-*Me*), 2.38, 2.28, 2.00 s, (9H, $Me_2C_6H_3$ + C(*Me*)=CH_2). ^{13}C NMR ($CDCl_3$, 293 K) Isomer *Z*: δ 227.3 (μ-*C*O), 221.4 (C_α-N), 198.2 (*C*O), 194.6 (C_γ), 156.9 (*C*-ipso Xyl), 134.0, 133.2 (*C*-Me Xyl), 129.7–128.9 (*C*H Xyl), 123.0 (*C*(Me)=CH_2), 111.4 (C(Me)=*C*H$_2$), 93.8, 89.1 (*Cp*), 60.6 (C_β), 47.1 (N-*Me*), 26.9 (C(*Me*)=CH_2), 18.0, 17.8 ($Me_2C_6H_3$).

4.9. Synthesis of [$Ru_2\{\mu$-η^1:η^3C(CO_2Me)=C(CO_2Me)C=N(Me)(Bz)$\}(\mu$-CO)(CO)$(Cp)_2$] [SO_3CF_3] (**11**)

A solution of **1b** (0.085 mmol) and $MeO_2CC{\equiv}CCO_2Me$ (0.100 mL, 0.708 mmol) in THF (12 mL) was refluxed for 1 h. After removal of the solvent in vacuo, the residue was washed with petroleum ether (3 × 5 mL) and Et_2O (3 × 5 mL), dissolved in CH_2Cl_2 (5 mL), filtered through celite and dried in vacuo affording the final product as an yellow-orange powder. Yield: 58.6 mg (86%). Anal. Calc. for $C_{28}H_{26}F_3NO_9Ru_2S$: C, 41.43; H, 3.23, N, 1.73. Found: C, 41.22; H, 3.12, N, 1.89. IR (CH_2Cl_2, 293 K): *v* (cm^{-1}) 2004vs (CO), 1838s (μ-CO), 1737vs, 1726sh (COOMe), 1670ms (C=N). ^{1}H NMR ($CDCl_3$, 293 K) Isomer *E*: δ 7.50–7.20 (m, 5H, *Ph*), 5.62, 5.51 (s, 10H, *Cp*), 5.10 (d, $^2J_{HH} = 15.9$ Hz, 1H, C*H*$_2$Ph. Second doublet hidden by Cp), 4.01, 3.88 (s, 9H, N-*Me* + CO_2Me); Isomer *Z*: δ 7.50–7.20 (m, 5H, *Ph*), 5.59, 5.57 (s, 10H, *Cp*), 5.04, 4.48 (d, $^2J_{HH} = 14.1$ Hz, 2H, C*H*$_2$Ph), 4.00, 3.88 (s, 6H, CO_2Me), 3.23 (s, 3H, N-*Me*). Isomer ratio *E*/*Z* = 2.2. ^{13}C NMR ($CDCl_3$, 293 K) Isomer *E*: δ 225.4 (μ-*C*O), 212.0

(C_α-N), 196.0 (*C*O), 175.0 (C_γ), 170.6, 166.2 (*C*O_2Me), 131.7 (*C*-ipso Ph), 129.5, 129.3, 128.6 (*C*H Ph), 93.2, 91.1 (*Cp*), 63.5 (*C*H_2Ph), 58.9 (C_β), 53.9, 53.1 (CO_2*Me*), 47.7 (N*Me*); Isomer *Z*: δ 224.7 (μ-*C*O), 212.6 (C_α-N), 196.5 (*C*O), 175.0 (C_γ), 169.9, 165.1 (*C*O_2Me), 130.8 (*C*-ipso Ph), 129.5, 129.0, 128.6 (*C*H Ph), 93.1, 91.3 (*Cp*), 67.7 (*C*H_2Ph), 59.6 (C_β), 53.8, 52.9 (CO_2*Me*), 44.2 (N-*Me*).

4.10. Synthesis of [Ru_2{μ-η¹:η³C(Et)=C(Et)C=N(Me)-(R)}(μ-CO)(CO)(Cp)$_2$][SO_3CF_3] (R = Xyl, **12a**; R = Bz, **12b**)

A solution of **1a**,**b** (0.100 mmol) and EtC≡CEt (0.100 mL, 0.868 mmol) in THF (10 mL) was refluxed for 1 h affording an orange solution. Hence, the solvent was removed under reduced pressure and the residue dissolved in CH_2Cl_2 (5 mL) and chromatographed through a Al_2O_3 column. The final product was obtained as an orange fraction using CH_3CN as eluent.

12a: Yield: 55.1 mg (72%). Anal. Calc. for $C_{29}H_{32}F_3NO_5Ru_2S$: C, 45.49; H, 4.21, N, 1.83. Found: C, 45.32; H, 4.38, N, 1.7. IR (CH_2Cl_2, 293 K): *v* (cm^{-1}) 1984vs, 1925s (CO), 1616m, 1587w (C=N). ^{1}H NMR ($CDCl_3$, 293 K) Isomer *cis*: δ 7.40–7.12 (m, 3H, *arom*), 5.64, 5.08 (s, 10H, *Cp*), 3.55 (s, 3H, N-*Me*), 3.88–3.51, 2.77–2.12 (m, 4H, γ-CH_2CH$_3$ + β-CH_2CH$_3$), 2.41, 2.04 (s, 6H, *Me*$_2$C$_6$H$_3$), 1.54 (t, $^3J_{HH}$ = 7.4 Hz, 3H, γ-CH$_2$C*H*$_3$), 1.35 (t, $^3J_{HH}$ = 7.7 Hz, 3H, β-CH$_2$C*H*$_3$); Isomer *trans*: δ 7.40–7.12 (m, 3H, *arom*), 5.30, 4.87 (s, 10H, *Cp*), 3.72 (s, 3H, N-*Me*), 3.88–3.51, 2.77–2.12 (m, 4H, γ-CH_2CH$_3$ + β-CH_2CH$_3$), 1.46 (t, $^3J_{HH}$ = 7.4 Hz, 3H, γ-CH$_2$C*H*$_3$), 1.35 (t, $^3J_{HH}$ = 7.7 Hz, 3H, β-CH$_2$C*H*$_3$); Isomer ratio *cis*/*trans* = 2.5. ^{13}C NMR ($CDCl_3$, 293 K) Isomer *cis*: δ 228.2 (μ-*C*O), 221.9 (C_α-N), 199.4 (*C*O), 193.7 (C_γ), 140.9–122.9 (arom), 92.5, 89.2 (*Cp*), 79.0 (C_β), 49.0 (N-*Me*), 42.6 (γ-*C*H$_2$CH$_3$), 24.2 (β-*C*H$_2$CH$_3$), 20.6, 16.4 (γ-CH$_2$*C*H$_3$ + β-CH$_2$*C*H$_3$), 18.3, 18.2 (*Me*$_2$C$_6$H$_3$); Isomer *trans*: 226.8 (μ-*C*O), 218.5 (C_α-N), 199.4 (*C*O), 194.8 (C_γ), 140.9–122.9 (arom), 91.1, 89.9 (*Cp*), 79.0 (C_β), 49.2 (N-*Me*), 41.9 (γ-*C*H$_2$CH$_3$), 25.9 (β-*C*H$_2$CH$_3$), 20.7, 15.6 (γ-CH$_2$*C*H$_3$ + β-CH$_2$*C*H$_3$), 18.2, 18.0 (*Me*$_2$C$_6$H$_3$).

Note. If the mixture of *cis*- and *trans*-**12a** is further refluxed for ca. 5 h, pure *cis*-**12a** is obtained.

12b: Yield: 58.6 mg (78%). Anal. Calc. for $C_{28}H_{30}F_3NO_5Ru_2S$: C, 44.73; H, 4.02, N, 1.86. Found: C, 44.12; H, 3.87, N, 2.01. IR (CH_2Cl_2, 293 K): *v* (cm^{-1}) 1986vs, 1816s (CO), 1653ms (C=N). ^{1}H NMR ($CDCl_3$, 293 K) Isomer *E*: δ 7.40–7.11 (m, 5H, *Ph*), 5.58, 5.38 (s, 10H, *Cp*), 4.80, 4.41 (d, $^2J_{HH}$ = 14.6 Hz, 2H, CH_2Ph), 3.58 (m, 2H, γ-CH_2CH$_3$), 3.46 (s, 3H, N-*Me*), 2.28 (m, 2H, β-CH_2CH$_3$), 1.44 (t, 3H, $^3J_{HH}$ = 7.4 Hz, γ-CH$_2$C*H*$_3$), 1.06 (t, $^3J_{HH}$ = 7.6 Hz, 3H, β-CH$_2$C*H*$_3$); Isomer *Z*: δ 7.40–7.11 (m, 5H, *Ph*), 5.60, 5.36 (s, 10H, *Cp*), 5.34, 4.90 (d, $^2J_{HH}$ = 14.3 Hz, 2H, CH_2Ph), 3.58 (m, 2H, γ-CH_2CH$_3$), 3.00 s, (3H, N-*Me*), 2.28 (m, 2H, β-CH_2CH$_3$), 1.16 (t, 3H, $^3J_{HH}$ = 7.4 Hz, γ-CH$_2$C*H*$_3$), 0.92 (t, $^3J_{HH}$ = 7.6 Hz, 3H, β-CH$_2$C*H*$_3$); Isomer ratio *E*/*Z* = 2. ^{13}C NMR ($CDCl_3$, 293 K) Isomer *E*: δ 231.7 (μ-*C*O), 219.8 (C_α-N), 198.9 (*C*O), 191.3 (C_γ), 131.2 (C-ipso Ph), 129.4–128.3 (CH arom), 92.2, 89.0 (*Cp*), 78.8 (C_β), 65.6 (*C*H_2Ph), 43.5 (N-*Me*), 43.0 (γ-*C*H$_2$CH$_3$), 23.0 (β-*C*H$_2$CH$_3$), 20.0, 15.9 (CH$_2$*C*H$_3$); Isomer *Z*: δ 232.7 (μ-*C*O), 218.2 (C_α-N), 198.3 (*C*O), 191.0 (C_γ), 132.2 (C-ipso Ph), 129.4–128.3 (CH arom), 92.4, 88.8 (*Cp*), 79.1 (C_β), 63.0 (*C*H_2Ph), 45.1 (N-*Me*), 43.0 (γ-*C*H$_2$CH$_3$), 22.1 (β-*C*H$_2$CH$_3$), 19.1, 15.2 (CH$_2$*C*H$_3$).

4.11. Synthesis of [Ru_2{μ-η¹:η³C(Me)=C(Me)C=N(Me)(Xyl)}(μ-CO)(CO)(Cp)$_2$][SO_3CF_3] (**13**)

$AgSO_3CF_3$ (25.0 mg, 0.097 mmol) was added to a solution containing **8** (34.1 mg, 0.060 mmol) and MeC≡CMe (0.6 mL, 7.67 mmol) in CH_2Cl_2 (5 mL) at −50 °C. After stirring at room temperature for 3 h, the mixture was filtered through Al_2O_3 using CH_3CN in order to remove AgCl. Hence, 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 a bright orange fraction using CH_3CN as eluent. Yield: 28.3 mg (64%). Found: C, 44.12; H, 3.67, N, 2.01. $C_{27}H_{28}F_3NO_5Ru_2S$ requires: C, 43.97; H,. 3.83%, N, 1.90%. Colour: orange. IR (in DCM, 293 K) *v* (cm^{-1}) Isomer *cis*: 1984vs (CO), 1825s (μ-CO), 1617ms, 1588m (C=N); Isomer *trans*: 1988vs (CO), 1831s (μ-CO), 1613ms, 1587m (C=N). ^{1}H NMR ($CDCl_3$, 293 K) Isomer *cis*: 7.64–7.08 (m, 3H, *arom*), 5.65, 5.06 (s, 10H, *Cp*), 3.58, 3.52 (s, 6H, N-*Me* + γ-CH_3), 2.39, 2.04 (s, 6H, *Me*$_2$C$_6$H$_3$), 2.16 (s, 3H, β-CH_3); Isomer *trans*: 7.32–6.92 (m, 3H, *arom*), 5.24, 4.78 (s, 10H, *Cp*), 3.65, 3.46 (s, 6H, N-*Me* + γ-CH_3), 2.29, 1.97 (s, 6H, *Me*$_2$C$_6$H$_3$), 2.17 (3H, β-CH_3). Isomer ratio *trans*/*cis* = 1.3. ^{13}C NMR ($CDCl_3$, 293 K) Isomer *cis*: 228.7 (μ-*C*O), 222.3 (C_α-N), 199.2 (*C*O), 184.5 (C_γ), 141.2 (*C*-ipso Xyl), 133.9, 133.8 (*C*-Me Xyl), 130.2–129.1 (*C*H Xyl), 93.1, 89.6 (*Cp*), 74.8 (C_β), 48.7 (N-*Me*), 38.5 (γ-*C*H$_3$), 18.3, 18.2, 17.7 (β-*C*H$_3$ + *Me*$_2$C$_6$H$_3$); Isomer *trans*: 227.3 (μ-*C*O), 219.32 (C_α–N), 1995.1 (*C*O), 179.3 (C_γ), 142.3 (*C*-ipso Xyl), 133.8, 132.9 (*C*-Me Xyl), 130.2–129.1 (*C*H Xyl), 91.4, 89.8 (*Cp*), 80.6 (C_β), 48.5 (N-*Me*), 38.5 (γ-*C*H$_3$), 18.2, 18.1, 18.0 (β-*C*H$_3$ + *Me*$_2$C$_6$H$_3$).

Note. If the mixture of *cis*- and *trans*-**13** is refluxed for ca. 5 h in THF, pure *cis*-**13** is obtained.

4.12. Synthesis of [Ru_2{μ-η¹:η³C(R′)C(R″)=C(H)N-(Me)(R)}(μ-CO)(CO)(Cp)$_2$] (R = Bz, R′ = Me_3Si, R″ = H, **14a**; R = Me, R′ = Me_3Si, R″ = H, **14b**; R = Bz, R′ = Tol, R″ = H, **15**; R = Bz, R′ = R″ = Et, **16**)

$NaBH_4$ (9.00 mg, 0.237 mmol) was added to a solution of **2b**,**c**, **3b** or **12b** (0.100 mmol), respectively, in THF (10 mL). After stirring 30 min at room temperature, MeOH (5 mL) was added and the solution further stirred for 15 min in order to destroy unreacted $NaBH_4$. The resulting suspension was filtered through a Al_2O_3 pad and the solvent removed in vacuum from the filtrated.

The residue was, then, dissolved in CH_2Cl_2 (5 mL) and chromatographed through Al_2O_3. The product was obtained as an orange fraction using CH_2Cl_2 eluent.

14a: Yield: 47.1 mg (76%). Anal. Calc. for $C_{26}H_{31}NO_2Ru_2Si$: C, 50.39; H, 5.04, N, 2.26. Found: C, 50.04; H, 5.12, N, 2.56. IR (CH_2Cl_2, 293 K): ν (cm^{-1}) 1928vs, 1760s (CO). ^1H NMR ($CDCl_3$, 293 K): δ 7.45–7.21 (m, 5H, *Ph*), 5.20, 5.01 (s, 10H, *Cp*), 4.38 (d, $^3J_{HH} = 8.79$ Hz, 1H, C_β-*H*), 3.81, 3.53 (d, $^2J_{HH} = 14.28$ Hz, 2H, CH_2Ph), 2.75 (d, $^3J_{HH} = 8.79$ Hz, 1H, C_α-*H*), 2.14 (s, 3H, N*Me*), 0.29 (s, 9H, Si*Me*$_3$). $^{13}C\{^1H\}$ ($CDCl_3$, 293 K): δ 254.4 (μ-*C*O), 205.9 (*C*O), 156.6 (μ-*C*γ), 137.5 (*C*-ipso arom), 128.7, 128.3, 127.2 (*C*H arom), 105.2 (C_α-H), 87.6, 81.4 (Cp), 69.2 (C_β-H), 61.2 (CH_2Ph), 37.8 (N*Me*), 2.8 (Si*Me*$_3$).

14b: Yield: 34.4 mg (67%). Anal. Calc. for $C_{20}H_{27}NO_2Ru_2Si$: C, 44.19; H, 5.01, N, 2.58. Found: C, 44.34; H, 5.15, N, 2.38. IR (CH_2Cl_2, 293 K): ν (cm^{-1}) 1948vs, 1784s (CO). ^1H NMR ($CDCl_3$, 293 K): δ 5.26, 5.02 (s, 10H, *Cp*), 4.30 (d, $^3J_{HH} = 8.6$ Hz, 1H, C_β-*H*), 2.19 (s, 6H, N*Me*$_2$), 2.53 (d, $^3J_{HH} = 8.6$ Hz, 1H, C_α-*H*).

15: Yield: 56.8 mg (89%). Anal. Calc. for $C_{30}H_{29}NO_2Ru_2$: C, 56.50; H, 4.58, N, 2.20. Found: C, 56.97; H, 4.12, N, 2.77. IR (CH_2Cl_2, 293 K): ν (cm^{-1}) 1931vs, 1760s (CO). ^1H NMR ($CDCl_3$, 293 K): δ 7.08–7.40 (m, 9H, *Ph* + *Tol*), 5.09, 4.94 (s, 10H, *Cp*), 4.25 (d, $^3J_{HH} = 8.8$ Hz, 1H, C_β-*H*), 3.82, 3.59 (d, $^2J_{HH} = 14.3$ Hz, 2H, CH_2Ph), 2.82 (d, $^3J_{HH} = 8.8$ Hz, 1H, C_α-*H*), 2.36, 2.15 (6H, s, N*Me* + *p*-*Me*C_4H_6). $^{13}C\{^1H\}$ ($CDCl_3$, 293 K): δ 245.4 (μ-*C*O), 205.5 (*C*O), 161.9 (μ-C_γ), 155.2, 137.4, 134.2 (*C*-ipso *Ph* + *Tol*), 129.0, 128.6, 128.3, 128.0, 127.2 (*C*H *Ph* + *Tol*), 102.1 (C_α-H), 89.8, 83.0 (*Cp*), 67.20 (C_β-H), 61.3 (CH_2Ph), 37.5 (N*Me*), 21.0 (*Me*C_4H_6).

16: Yield: 53.1 mg (88%). Anal. Calc. for $C_{27}H_{31}NO_2Ru_2$: C, 53.71; H, 5.17, N, 2.32. Found: C, 53.15; H, 5.32, N, 2.06. IR (CH_2Cl_2, 293 K): ν (cm^{-1}) 1938vs, 1787s (CO). ^1H NMR ($CDCl_3$, 293 K): δ 7.62–7.10 (m, 5H, *Ph*), 5.14, 4.75 (s, 10H, *Cp*), 3.96, 3.48 (d, $^2J_{HH} = 14.1$ Hz, 2H, CH_2Ph), 3.74, 3.20 (dq, $^2J_{HH} = 13.0$ Hz, $^3J_{HH} = 7.4$ Hz, 2H, α-CH_2CH_3), 2.48, 2.29 (dq, $^2J_{HH} = 13.6$ Hz, $^3J_{HH} = 7.5$ Hz, 2H, β-CH_2CH_3), 2.15 (s, 3H, N*Me*), 1.37 (t, $^3J_{HH} = 7.3$ Hz, 3H, α-CH_2CH_3), 1.16 (t, $^3J_{HH} = 7.5$ Hz, 3H, β-CH_2CH_3), 0.92 (s, 1H, C_α-*H*). $^{13}C\{^1H\}$ ($CDCl_3$, 293 K): δ 246.4 (μ-*C*O), 205.8 (*C*O), 179.5 (μ-C_γ), 139.9 (*C*-ipso *Ph*), 130.9, 128.8, 128.3, 128.2, 126.6 (*C*H *Ph*), 96.1 (C_α-H), 94.4 (C_β-Et), 89.2, 85.5 (*Cp*), 65.9 (CH_2Ph), 44.5 (N*Me*), 43.2, 23.9 (CH_2CH_3), 21.4, 16.3 (CH_2CH_3).

*4.13. Synthesis of [Ru_2{μ-η^1:η^2-C(R′)C(H)(R″)CN(Me)-(Xyl)}(μ-CO)(CO)(Cp)$_2$] (R′ = Me_3Si, R″ = H, **17**; R′ = R″ = Et, **18**)*

$NaBH_4$ (12.0 mg, 0.316 mmol) was added to a solution of **2a** or **12b** (0.100 mmol) in THF (6 mL) and stirred at room temperature for 2 h. Hence, MeOH (0.4 mL) was added and the solution further stirred for 20 min. The solvent was then removed in vacuo and the residue dissolved in CH_2Cl_2 (5 mL) and filtered through Al_2O_3, affording a yellow-orange solution, from which the product was obtained after chromatography through a Al_2O_3 column using CH_2Cl_2 as eluent.

17: Yield: 48.9 mg (77%). Anal. Calc. for $C_{27}H_{34}NO_2Ru_2Si$: C, 51.09; H, 5.40, N, 2.21. Found: C, 51.16; H, 5.30; N, 2.33. IR (CH_2Cl_2, 293 K): ν (cm^{-1}) 1918vs, 1747s (CO), 1515m (C=N). ^1H NMR ($CDCl_3$, 293 K) Isomer *E*: δ 7.26–6.98 (m, 3H, *arom*), 5.21, 5.06 (s, 10H, *Cp*), 4.05, 3.68 (d, $^2J_{HH} = 20.4$ Hz, 2H, $C_\beta H_2$), 3.70 (s, 3H, N-*Me*), 2.02 (s, 6H, *Me*$_2C_6H_3$), 0.18 (s, 9H, $SiMe_3$); Isomer *Z*: δ 7.26–6.98 (m, 3H, *arom*), 5.17, 5.01 (s, 10H, *Cp*), 4.16, 3.76 (d, $^2J_{HH} = 20.4$ Hz, 2H, $C_\beta H_2$), 3.72 (s, 3H, N-*Me*), 2.08 (s, 6H, *Me*$_2C_6H_3$), 0.20 (s, 9H, $SiMe_3$). Isomer ratio *E*/*Z* = 13. $^{13}C\{^1H\}$ (in $CDCl_3$, 293 K) Isomer *E*: δ 252.7 (μ-*C*O), 247.2 (C_α), 206.3 (*C*O), 142.3 (*C*-ipso Xyl), 135.1, 132.7, 131.7 (μ-*C*γ + *C*-Me Xyl), 128.9, 128.3, 128.0 (*C*H Xyl), 87.2, 85.6 (*Cp*), 69.6 ($C_\beta H_2$), 47.5 (N*Me*), 17.5, 17.2 (*Me*$_2C_6H_3$), 2.4 (Si*Me*$_3$); Isomer *Z*: δ 87.5, 85.4 (*Cp*), 70.8 ($C_\beta H_2$), 47.5 (N*Me*), 18.0, 17.9 (*Me*$_2C_6H_3$), 2.2 (Si*Me*$_3$).

18: Yield: 43.9 mg (71%). Anal. Calc. for $C_{28}H_{33}NO_2Ru_2$: C, 54.44; H, 5.38, N, 2.27. Found: C, 54.28; H, 5.45; N, 2.18. IR (CH_2Cl_2, 293 K): ν (cm^{-1}) 1905vs, 1757s (CO), 1508m (C=N). ^1H NMR ($CDCl_3$, 293 K) Isomer *cis*-*Z*: δ 7.29–6.93 (m, 3H, *arom*), 5.14, 4.59 (s, 10H, *Cp*), 3.65, 3.26 (dq, $^2J_{HH} = 13.0$ Hz, $^3J_{HH} = 7.3$ Hz, 2H, γ-CH_2CH_3), 3.20 (m, 1H, $C_\beta H$), 3.16 (s, 3H, N-*Me*), 2.27, 2.24 (s, 6H, *Me*$_2C_6H_3$), 1.50, 1.30 (m, 2H, β-CH_2CH_3), 1.40 (t, $^3J_{HH} = 7.3$ Hz, 3H, γ-CH_2CH_3), 1.25 ($^3J_{HH} = 7.6$ Hz, 3H, β-CH_2CH_3); Isomer *trans*-*Z*: δ 7.29–6.93 (m, 3H, *arom*), 5.23, 4.93 (s, 10H, *Cp*), 3.80, 3.30 (m, 2H, γ-CH_2CH_3), 3.40 (m, 1H, $C_\beta H$), 2.94 (s, 3H, N-*Me*), 2.30, 2.26 (s, 6H, *Me*$_2C_6H_3$), 2.40, 1.90 (m, 2H, β-CH_2CH_3), 1.45 (t, $^3J_{HH} = 7.1$ Hz, 3H, γ-CH_2CH_3), 0.73 ($^3J_{HH} = 7.5$ Hz, 3H, β-CH_2CH_3). Isomer ratio *cis*-*Z*/*trans*-*Z* = 5. $^{13}C\{^1H\}$ (in $CDCl_3$, 293 K) Isomer *cis*-*Z*: δ 257.6 (C_α), 251.4 (μ-*C*O), 207.3 (*C*O), 160.5 (μ-C_γ), 146.1 (*C*-ipso Xyl), 134.7, 133.4 (*C*-Me Xyl), 129.5, 127.90 127.6 (*C*H Xyl), 89.4, 86.5 (*Cp*), 82.1 (C_βH), 46.4, 26.1 (β + γ-CH_2CH_3) 41.0 (NMe), 19.2, 18.2, 17.8, 14.5 (*Me*$_2C_6H_3$ + β + γ-CH_2CH_3); Isomer *trans*-*Z*: δ 256.7 (C_α), 251.6 (μ-*C*O), 206.2 (*C*O), 160.1 (μ-C_γ), 146.1 (*C*-ipso Xyl), 136.3, 136.1 (*C*-Me Xyl), 130–127 (*C*H Xyl), 89.1, 85.0 (*Cp*), 84.4 (C_βH), 44.9, 24.1 (β + γ-CH_2CH_3) 40.4 (N*Me*), 21.3, 20.2, 19.8, 14.0 (*Me*$_2C_6H_3$ + β + γ-CH_2CH_3).

*4.14. Synthesis of [Ru_2{μ-CN(Me)(R)}(μ-CO)(CO)-(CCR′)(Cp)$_2$] (R = Xyl, R′ = Tol, **19**; R = Bz, R′ = Me_3Si, **20**; R = Xyl, R′ = Me, **21**)*

NaH (10.0 mg, 0.417 mmol) was added to a solution of **3a**, **2b** and **7** (0.100 mmol), respectively, in THF (10 mL). After stirring 30 min at room temperature, MeOH (5 mL) was added and the solution further stirred for 15 min in order to eliminate unreacted NaH. The resulting suspension was filtered through a celite pad and the solvent removed in vacuum from the filtrated. The residue was,

then, washed with petroleum ether (3 × 15 mL) and dried in vacuum affording the final product as an orange powder.

19: Yield: 39.6 mg (61%). Anal. Calc. for $C_{31}H_{29}NO_2Ru_2$: C, 57.31; H, 4.50, N, 2.16. Found: C, 57.22; H, 4.62, N, 2.09. IR (CH_2Cl_2, 293 K): ν (cm^{-1}) 2094s (C≡C), 1966vs, 1795s (CO), 1516ms (C=N). ^1H NMR ($CDCl_3$, 293 K): δ 7.22–7.11 (m, 3H, *Xyl*), 6.97, 6.83 (d AB, $^3J_{HH} = 7.9$, 4H, *p*-C_6H_4Me), 5.30, 4.81 (s, 10H, *Cp*), 4.07 (s, 3H, N-*Me*), 2.37, 2.24, 2.19 (s, 9H, $Me_2C_6H_3$ + *p*-C_6H_4Me). $^{13}C\{^1H\}$ ($CDCl_3$, 293 K): δ 310.1 (μ-*C*), 235.2 (μ-*C*O), 201.9 (*C*O), 148.0 (*C*-ipso Xyl), 133.8, 133.1, 132.8 (*C*-Me Xyl + Tol), 130.8–127.8 (*C*H Xyl + Tol), 107.2, 98.5 (*C*≡*C*), 89.0, 87.7 (*Cp*), 50.8 (N*Me*), 21.2 (*p*-C_6H_4Me), 18.3, 17.4 ($Me_2C_6H_3$).

20: Yield: 42.0 mg (68%). Anal. Calc. for $C_{26}H_{29}NO_2Ru_2Si$: C, 50.55; H, 4.73, N, 2.27. Found: C, 51.05; H, 4.89, N, 2.42. IR (CH_2Cl_2, 293 K): ν (cm^{-1}) 2022s (C≡C), 1969vs, 1798s (CO), 1547ms (C=N). ^1H NMR ($CDCl_3$, 293 K) Isomer α: δ 7.30–7.50 (m, 5H, *Ph*), 5.49, 5.34 (d, $^2J_{HH} = 14.8$ Hz, 2H, CH_2Ph), 5.23, 5.16 (s, 10H, *Cp*), 3.73 (s, 3H, N-*Me*), −0.07 (s, 9H, SiMe_3); Isomer β: δ 7.30–7.50 (m, 5H, *Ph*), 5.95, 5.55 (d, $^2J_{HH} = 15.4$ Hz, 2H, CH_2Ph), 5.25, 5.10 (s, 10H, *Cp*), 3.67 (s, 3H, N-*Me*), −0.05 (s, 9H, SiMe_3). Isomer ratio α/β = 1.7. $^{13}C\{^1H\}$ ($CDCl_3$, 293 K) Isomer α: δ 308.9 (μ-*C*), 239.8 (μ-*C*O), 201.5 (*C*O), 134.9 (*C*-ipso Ph), 129.1, 128.2, 127.0 (*C*H Ph), 111.7, 94.1 (*C*≡*C*), 89.1, 87.8 (*Cp*), 69.4 (*C*H_2Ph), 47.5 (N*Me*), 1.6 (SiMe_3); Isomer β: δ 307.2 (μ-*C*), 235.5 (μ-*C*O), 201.4 (*C*O), 135.5 (*C*-ipso Ph), 129.1, 128.0, 127.3 (*C*H Ph), 111.9, 94.4 (*C*≡*C*), 90.0, 87.9 (*Cp*), 68.3 (*C*H_2Ph), 49.4 (N*Me*), 1.5 (SiMe_3).

21: Yield: 39.0 mg (68%). Anal. Calc. for $C_{25}H_{25}NO_2Ru_2$: C, 53.35; H, 4.39; N, 2.44. Found: C, 57.22; H, 4.62, N, 2.09. IR (in DCM, 293 K) ν (cm^{-1}): 2123w (C≡C), 1962vs (CO), 1792s (μ-CO), 1516ms (C=N). ^1H NMR ($CDCl_3$, 293 K): δ 7.11 (m, 3H, *Xyl*), 5.18, 4.74 (s, 10H, *Cp*), 3.99 (s, 3H, N-*Me*), 2.32, 2.23 (s, 6H, $Me_2C_6H_3$), 1.65 (s, 3H, *Me*). $^{13}C\{^1H\}$ ($CDCl_3$, 293 K): δ 310.7 (μ-*C*), 236.4 (μ-*C*O), 202.8 (*C*O), 148.3 (*C*-ipso Xyl), 133.9, 133.2 (*C*-Me Xyl), 129.9, 128.3, 128.1 (*C*H Xyl), 99.4, 84.6 (*C*≡*C*), 88.8, 87.9 (*Cp*), 51.0 (N*Me*), 18.5, 17.2 ($Me_2C_6H_3$), 6.3 (*Me*).

4.15. Synthesis of [Ru_2{μ-η^3:η^1-C[N(Me)(Xyl)]C(H)C=CH_2}(μ-CO)(CO)(Cp_2)] (**22**)

Complex **21** (100.0 mg, 0.174 mmol) was dissolved in CH_2Cl_2 (5 mL) and transferred on top of a Al_2O_3 column. Product **22** was obtained as an orange fraction using CH_2Cl_2 as eluent. Yield: 54.2 mg (54%). Anal. Calc. for $C_{25}H_{25}NO_2Ru_2$: C, 52.35; H, 4.39, N, 2.44. Found: C, 52.68; H, 4.11, N, 2.15. IR (in CH_2Cl_2 293 K) ν (cm^{-1}): 1953vs (CO), 1769s (μ-CO). ^1H NMR ($CDCl_3$, 293 K): δ 7.14–7.08 (m, 3H, *Xyl*), 5.22, 4.92 (br, 2H, CH_2), 5.48, 5.06 (s, 10H, *Cp*), 3.72 (s, 1H, C_β-*H*), 3.27 (s, 3H, N-*Me*), 2.67, 2.56 (s, 6H, $Me_2C_6H_3$). $^{13}C\{^1H\}$ ($CDCl_3$, 298 K): δ 243.0 (μ-*C*O), 203.1 (*C*O), 187.6 (C_γ), 165.7 (C_α), 149.6 (*C*-ipso Xyl), 136.2, 135.9 (*C*-Me Xyl), 129.7, 128.5, 126.7 (*C*H $Me_2C_6H_3$), 103.4 (*C*H_2), 87.8, 85.0 (*Cp*), 48.7 (C_β), 45.9 (N-*Me*), 20.2, 18.9 ($Me_2C_6H_3$).

4.16. Synthesis of [Ru_2{μ-η^1:η^2-C(Me)CCN(Bz)(Me)}(μ-CO)(CO)($Cp)_2]_2$ (**23**)

NaH (125.1 mg, 5.21 mmol) was added to a solution of **7b** (352.2 mg, 0.496 mmol) in THF (20 mL). The resulting suspension was stirred at room temperature for 40 min and, then, filtered through a Al_2O_3 pad. After removal of the solvent from the filtrated, the residue was chromatographed through Al_2O_3; the final product was obtained as a green fraction using CH_2Cl_2/THF (3:1) as eluent. Yield: 147.1 mg (53%). Anal. Calc. for $C_{48}H_{46}N_2O_4Ru_4$: C, 51.51; H, 4.14, N, 2.50. Found: C, 51.89; H, 3.85, N, 2.15. IR (in CH_2Cl_2, 293 K) ν (cm^{-1}): 1918vs (CO), 1738vs (CO), 1540m (CN). ^1H NMR ($CDCl_3$, 293 K): δ 7.66–7.00 (m, 5H, *Ph*), 5.25, 4.86 (s, 10H, *Cp*), 5.04, 4.69 (d, $^2J_{HH} = 14.8$ Hz, 2H, CH_2Ph), 3.37 (s, 3H, C_γ-*Me*), 2.35 (s, 6H, N-*Me*). $^{13}C\{^1H\}$ ($CDCl_3$, 293 K): δ 251.3 (μ-*C*O), 231.3 (C_α-N), 204.6 (*C*O), 157.5 (C_γ), 134.8 (*C*-ipso Ph), 129.6, 129.0, 128.5 (*C*H Ph), 89.0, 87.8 (*Cp*), 66.1 (*C*H_2), 64.9 (C_β), 46.5 (C_γ-*Me*), 38.6 (N-*Me*).

4.17. X-ray structural determinations

Compounds **2a**[CF_3SO_3] · 0.5CH_2Cl_2 and **12a**[CF_3SO_3] were crystallised from CH_2Cl_2/Et_2O, whereas compound **22** was crystallised from CH_2Cl_2/pentane. Crystal data were collected at room temperature on a Bruker AXS SMART 2000 CCD diffractometer using Mo Kα 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 matrixes 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 [18] was used for collecting frames of data, indexing reflections and determinations of lattice parameters. The collected frames were then processed for integration by the software SAINT and empirical absorption corrections were applied with SADABS [19]. The structure was solved by direct methods and refined by full-matrix least-squares based on all data using F^2 [20]. Crystal data are listed in Table 4. Non-H atoms were refined anisotropically, unless otherwise stated. H-atoms were placed in calculated positions, except positions of H(14) in **2a**[CF_3SO_3] · 0.5CH_2Cl_2 and H(14), H(16A), H(16B) in **22** which were located in the Fourier map and refined isotropically with thermal parameter 20% greater than that of the attached carbon. One Cp ligand, the $CF_3SO_3^-$ anion and the CH_2Cl_2 molecule in **2a**[CF_3SO_3] · 0.5CH_2Cl_2, one Cp ligand in **12a**[CF_3SO_3] and the two Cp ligands in **22** are disordered. Disordered atomic positions were split and refined isotropically using similar distance and similar *U* restraints and one occupancy parameter per disordered group.

Table 4
Crystal data and experimental details for **2a**[CF_3SO_3] · 0.5CH_2Cl_2, **12a**[CF_3SO_3] and **22**

Complex	**2a**[CF_3SO_3] · 0.5CH_2Cl_2	**12a**[CF_3SO_3]	**22**
Formula	$C_{28.5}H_{33}ClF_3NO_5Ru_2SSi$	$C_{29}H_{32}F_3NO_5Ru_2S$	$C_{25}H_{25}NO_2Ru_2$
F_w	824.30	765.76	573.60
T (K)	293(2)	293(2)	293(2)
λ, Å	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a (Å)	10.839(2)	8.2832(17)	8.7520(18)
b (Å)	17.836(4)	12.695(3)	15.631(3)
c (Å)	17.527(4)	15.101(3)	16.007(3)
α (°)	90	105.87(3)	90
β (°)	103.76(3)	102.36(3)	91.42(3)
γ (°)	90	90.72(3)	90
Cell volume (Å^3)	3290.9(11)	1487.8(5)	2189.1(8)
Z	4	2	4
D_c (g cm^{-3})	1.664	1.709	1.740
μ (mm^{-1})	1.153	1.143	1.401
F(000)	1652	768	1144
Crystal size (mm)	0.26 × 0.21 × 0.14	0.33 × 0.25 × 0.13	0.23 × 0.16 × 0.12
θ Limits (°)	1.65–25.03	1.44–25.03	1.82–27.10
Reflections collected	28655	13197	23022
Independent reflections [R_{int}]	5810 [0.0637]	5241 [0.0696]	4824 [0.0562]
Data/restraints/parameters	5810/100/391	5241/38/371	4824/127/275
Goodness on fit on F^2	1.042	0.987	1.027
R_1 ($I > 2\sigma(I)$)	0.0527	0.0584	0.0357
wR_2 (all data)	0.1500	0.1614	0.0932
Largest diff. peak and hole (e Å^{-3})	0.809/−0.946	1.154/−0.826	0.786/−0.537

Acknowledgements

We thank the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MIUR) (project: ''New strategies for the control of reactions: interactions of molecular fragments with metallic sites in unconventional species'') and the University of Bologna (''Funds for Selected Research Topics'') for financial support.

Appendix A. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 292588 for **2a**[CF_3SO_3] · 0.5CH_2Cl_2, 292589 for **22**, 292590 for **12a**[CF_3SO_3]. Copies of this information can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1233 336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.01.020.

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