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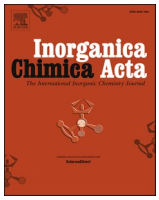

Ruthenium (0) complexes with NHC tetrazolylidene ligands: Synthesis, characterization and reactivity

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ABSTRACT

Here we present two new phenyl-tetrazolylidene carbenes as ligands in non-mesoionic (1,4-substitution pattern) and mesoionic (1,3-substitution pattern) tetrazolylidene-cyclopentadienone ruthenium(0) complexes namely **1** and **2** respectively. The complexes have been obtained in good yield and fully characterized; X-ray structure determination confirmed the binding mode of the ligand for **2**. Reactivity studies has been performed in order to shed light on the fact that the phenyl substituent position in the heterocyclic ligand can seriously change complexes behavior and stability.

1. Introduction

Since their discovery *N*-heterocyclic carbenes (NHCs) distinguished as versatile ligands in organometallic chemistry and a wide range of their applications can be found spanning from catalysis to materials, crossing over the organic synthesis [1–8].

The success of NHCs can be essentially ascribed to the relatively high covalent contribution to the M−NHC bond, and to their strong donor ability. In addition, the synthesis of NHC ligand precursors and of the corresponding complexes is generally rather simple and very versatile [9–12], allowing the rational design of metal complexes suitable for their final use [13–17]. Furthermore, the NHC-metal center bond is generally strong enough to form stable complexes.

By varying the number and the positions of heteroatoms in the ring, it is possible to obtain many structures of both normal (NHCs) and abnormal (aNHCs) or mesoionic (MIC) carbenes [18–20]. The latter are known to be stronger electron donors than normal carbenes.

Among NHCs containing multiple nitrogen atoms within the cycle, imidazolylidenes and 1,2,3-triazolylidenes have been widely investigated, both as single species and as ligands in organometallic complexes [3–8,21]. Conversely, tetrazolylidenes and the corresponding complexes still appear rarely in the literature [22–26].

The IUPAC definition of MIC is "Dipolar five- (possibly six-) membered heterocyclic compounds in which both the negative and the positive charge are delocalized, for which a totally covalent structure cannot be written, and which cannot be represented satisfactorily by any one polar structure. The formal positive charge is associated with the ring atoms, and the formal negative charge is associated with ring atoms or an exocyclic nitrogen or chalcogen atom" [27]. We can therefore state that the tetrazole ring with 1,4-substitution pattern (**a**) cannot be defined as MIC while the one with the 1,3-substitution pattern (**b**) can be defined as MIC (Fig. 1).

Another class of versatile ligands is represented by cyclopentadienones, which, exploiting the cyclopentadienone/hydroxycyclopentadienyl reversible transformation, behave as non-innocent ligands. The most famous example of cooperativity of such ligands in bifunctional catalysis is the Shvo catalyst, a well-known system employed in a plethora of catalytic applications [28–32].

Herein we report the first synthesis of non-mesoionic and mesoionic tetrazolylidene-cyclopentadienone ruthenium complexes, namely complexes **1** and **2** (Fig. 2), their characterization and their reactivity, evaluated with a few transfer hydrogenation reactions. Moreover, a comparison with previously reported complexes **3** [33,34] and **4** [35] containing carbenes with decreasing number of nitrogens respectively is discussed (Fig. 2).

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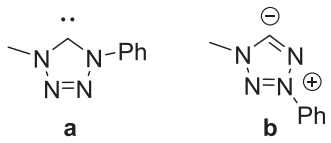


Fig. 1. Tetrazolylidene Ligands Presented in This Study.

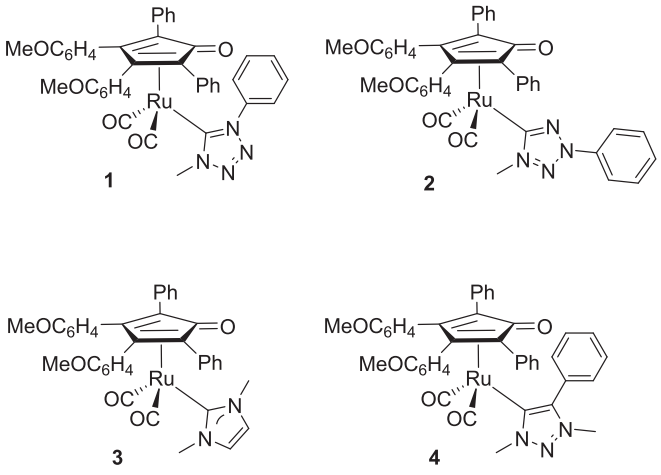


Fig. 2. Tetrazolylidene-Cyclopentadienone Ruthenium complexes **1** and **2** presented in this study in comparison with previously reported imidazolylidene **3** and triazolylidene **4** complexes.

2. Experimental section

2.1. General Information

Analytical grade solvents and commercially available reagents were used as received, unless otherwise stated. Chromatographic purifications were performed using 70–230 mesh silica or aluminum oxide. Solvents were dried and distilled according to standard procedures and stored under nitrogen. ^{1}H, ^{19}F and ^{13}C NMR spectra were recorded on a Varian Inova 300 MHz or on a Mercury 400 MHz spectrometer. Chemical shifts (δ) are reported in ppm relative to residual solvent signals for ^{1}H and ^{13}C NMR (^{1}H NMR: 7.26 ppm for $CDCl_3$, 1.94 ppm for CD_3CN; ^{13}C NMR: 77.0 ppm for $CDCl_3$, 1.32 ppm for CD_3CN). ^{19}F NMR spectra were recorded at 282 MHz using trichlorofluoromethane as external standard. ^{13}C NMR spectra were acquired with ^{1}H broad band decoupled mode. Coupling constants are given in Hertz. The high-resolution mass spectra (HRMS) were obtained with a Waters Q-TOF-MS instrument using electrospray ionization (ESI). Infrared spectra were recorded at 298 K on a PerkinElmer Spectrum Two FT-IR spectrophotometer. [3,4-(4-MeO-C_6H_4)$_2$–2,5-Ph_2(η^4-C_4CO)Ru-$(CO)_3$] has been prepared as previously reported.[36] NMR spectra of previously reported compounds were in agreement with those of the authentic samples and/or available literature data.

2.2. Synthesis of the ligands

Synthesis of 1-Phenyl-1*H*-tetrazole (**I**) [37]. Aniline (10 mmol, 0.91 mL, 1 eq.), sodium azide (11 mmol, 715 mg, 1.1 eq.) and triethyl orthoformate (30 mmol, 4.98 mL, 3 eq.) were dissolved in acetic acid (80 mmol, 4.58 mL, 8 eq.). The solution was heated at 80° C for 4 h under nitrogen atmosphere. After this time the reaction was quenched with brine (20 mL) and a saturated solution of Na_2CO_3 up to basic pH. The yellow solid obtained was filtered and washed several times with water (1.1 g, yield = 76 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 9.03 (s, 1H), 7.75–7.69 (m, 2H), 7.63–7.50 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 140.5 (CH), 133.8 (C), 130.2 (CH), 130.0 (CH), 121.2 (CH) [38].

Synthesis of 4-methyl-1-phenyl-1*H*-tetrazol-4-ium tetrafluoroborate (**II**). Compound **I** (1 mmol, 146 mg, 1 eq.) and Me_3OBF_4 (1.2 mmol, 180 mg, 1.2 eq.) was vigorously stirred in dry dichloromethane (9 mL) under nitrogen atmosphere at room temperature for 24 h. After this time, a mixture of isomers (95:5 ratio) of 4-methyl-1-phenyl-1*H*-tetrazol-4-ium tetrafluoroborate and 3-methyl-1-phenyl-1*H*-tetrazol-4-ium tetrafluoroborate was obtained. The crude was washed with diethyl ether and dichloromethane to give pure **II** as a white solid (136 mg, yield = 55 %). ^{1}H NMR (300 MHz, CD_3CN) δ: 10.53 (s, 1H), 7.90–7.84 (m, 2H), 7.82–7.74 (m, 3H), 4.45 (s, 3H); ^{13}C NMR (100 MHz, CD_3CN) δ: 142.4 (CH), 134.0 (CH), 133.7 (C), 132.1 (CH), 123.9 (CH), 39.4 (CH_3); ^{19}F NMR (282 MHz, CD_3CN) δ: 151.7. HRMS (ESI-QTOF) *m/z*: calcd. for $C_8H_9N_4$: 161.0822; found 161.0811 $[M-BF_4]^+$.

Synthesis of 2-phenyl-2*H*-tetrazole (**III**). In a round bottom flask aniline (9 mmol, 0.81 mL, 1 eq.), water (3.6 mL) and tetrafluoroboric acid solution 48 wt% in H_2O were mixed. The mixture was cooled to 0 °C in an ice bath and then a solution of $NaNO_2$ (9 mmol, 621 mg, 1 eq.) in 1.5 mL water was added slowly. After 30 min a white–pink solid was formed. The precipitate was collected by filtration and washed several times with diethyl ether to give the phenyldiazonium tetrafluroborate salt, which was dried under vacuum and used in the next step without further purifications. To a solution of formamidine hydrochloride (9 mmol, 725 mg, 1 eq.) and potassium carbonate (6.48 g, 46.8 mmol, 5.2 eq.) in DMSO (45 mL) was added phenyldiazonium tetrafluoroborate (9 mmol, 1 eq.) in portions. After stirring for 1 h at room temperature, a stirred solution of iodine (2.85 g, 11.25 mmol, 1.25 eq.) and potassium iodide (2.34 g, 14.04 mmol, 1.56 eq.) was added slowly and stirred for additional 1 h at room temperature. The reaction was quenched with $Na_2S_2O_3$ (10% w/v) and brine. The aqueous phase was extracted with ethyl acetate (3 times) and dried over Na_2SO_4. Product **III** was isolated by silica gel flash chromatography using a mixture of hexane/ethyl acetate (90:10) in 65% yield (859 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.66 (s, 1H), 8.18–8.12 (m, 2H), 7.62–7.48 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.9 (CH), 136.7 (C), 129.8 (CH), 129.6 (CH), 119.9 (CH) [39].

Synthesis of 4-methyl-2-phenyl-2H-tetrazol-4-ium tetrafluoroborate (**IV**). Compound **III** (3.4 mmol, 500 mg, 1 eq.) and Me_3OBF_4 (4.1 mmol, 612 mg, 1.2 eq.) was vigorously stirred in dry dichloromethane (35 mL) under nitrogen atmosphere at room temperature for 24 h. The crude was washed with diethyl ether to give pure **IV** as a brown solid (698 mg, yield = 83 %). ^{1}H NMR (400 MHz, CD_3CN) δ: 9.72 (s, 1H), 8.15–8.20 (m, 2H), 7.75–7.85 (m, 3H), 4.50 (s, 3H); ^{13}C NMR (100 MHz, CD_3CN) δ: 150.8 (CH), 136.6 (C), 135.1 (CH), 132.2 (CH), 122.7 (CH), 40.1 (CH_3); ^{19}F NMR (282 MHz, CD_3CN) δ: 151.9. HRMS (ESI-QTOF) *m/z*: calcd. for $C_8H_9N_4$: 161.0822; found 161.0807 $[M-BF_4]^+$.

2.3. Synthesis of ruthenium complexes *1* and *2*

General procedure: Ligand **II** or **IV** (0.17 mmol, 42 mg, 2 eq.) were dissolved in dry dichloromethane (15 mL) and the solution was stirred under nitrogen atmosphere. Then Ag_2O (0.18 mmol, 43 mg, 2.2 eq.) was added and the mixture stirred in absence of light. After 30 min, the ruthenium **Ru-dimer** was added (0.084 mmol, 100 mg, 1 eq.) and the mixture was stirred for additional 4 h. After this time the resulting solid was removed by filtration on a celite pad and the solvent was evaporated under reduced pressure. Column chromatography was performed in order to purify the product.

1: (stationary phase: aluminum oxide, eluent: hexane/ethyl acetate from 8:2 to 8:3; 114 mg; yield = 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.65–7.59 (m, 4H), 7.37–7.31 (m, 1H), 7.17–7.10 (m, 8H), 7.04–6.98 (m, 4H), 6.82 (d, J = 8.0 Hz, 2H), 6.59–6.55 (m, 4H), 3.67 (s, 3H), 3.66 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 200.4 (C), 174.8 (C), 171.1 (C), 158.7 (C), 135.8 (C), 134.3 (C), 133.4 (CH), 130.6 (CH), 129.5 (CH), 129.2 (CH), 127.7 (CH), 127.5 (CH), 125.9 (CH), 123.8 (C), 112.9 (CH), 104.2 (C), 79.5 (C), 55.0 (CH_3), 38.3 (CH_3). IR (CH_2Cl_2) νCO: 1962 cm^{-1}, 2017 cm^{-1}. HRMS (ESI-QTOF) *m/z*: calcd for $C_{41}H_{32}N_4O_5Ru$:

756.1449; found: 756.1431 $[M + H]^+$.

2: (stationary phase: aluminum oxide, eluent: hexane/ethyl acetate from 8:2 to 1:1; 98.5 mg; yield = 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.86–7.80 (m, 2H), 7.70–7.74 (m, 4H), 7.54–7.47 (m, 3H), 7.20–7.04 (m, 10*H*), 6.67–6.60 (m, 4H), 3.76 (s, 3H), 3.71 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 201.4 (C), 182.9 (C), 171.1 (C), 158.5 (C), 135.4 (C), 134.6 (C), 133.6 (CH), 131.5 (CH), 130.4 (CH), 129.8 (CH), 127.4 (CH), 125.6 (CH), 124.5 (C), 120.7 (CH), 112.8 (CH), 103.4 (C), 80.4 (C), 55.0 (CH_3), 37.9 (CH_3). IR (CH_2Cl_2) ν*CO*: 1955 cm^{-1}, 2014 cm^{-1}. HRMS (ESI-QTOF) *m/z*: calcd for $C_{41}H_{32}N_4O_5Ru$: 756.1449; found: 756.1437 $[M + H]^+$.

2.4. General procedure for catalytic transfer hydrogenation of 4-fluoroacetophenone

Ruthenium complex (0.015 mmol, 5 % mol) was dissolved in ^{i}PrOH (3 mL) and the resulting mixture was stirred at reflux for 15 min under nitrogen atmosphere. Then 4-fluoroacetophenone (0.036 mL, 0.3 mmol) was added and the mixture was refluxed again. Samples were taken at regular intervals (8 h and 24 h). Aliquots (ca. 0.05 mL) were diluted with $CDCl_3$ (0.5 mL) and the conversions were determined by ^{19}F NMR spectroscopy.

3. Results and discussion

3.1. Synthesis and characterization

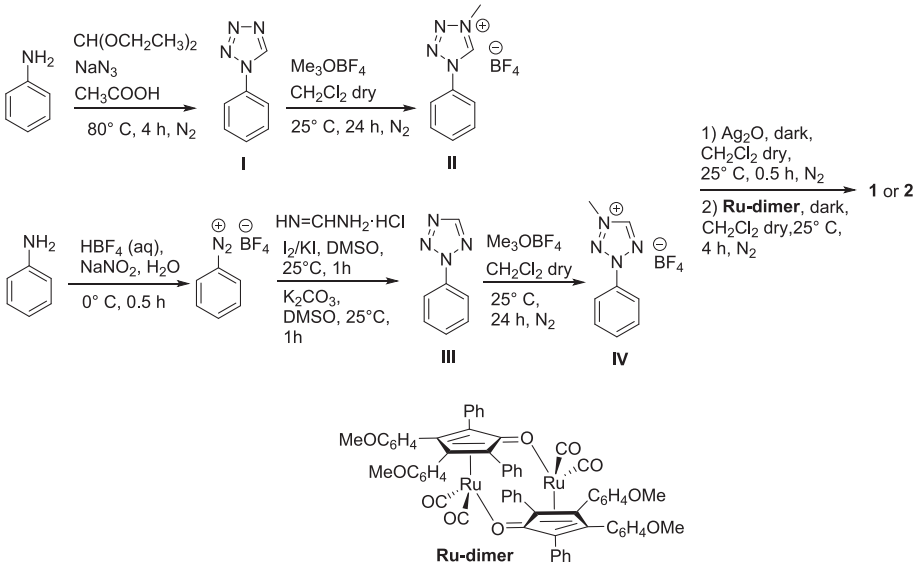
The precursors of tetrazolylidenes **II** and **IV** were synthesized following previously reported procedures (Scheme1). In detail, 1-phenyl-1*H*-tetrazole **I** [37], obtained from a one-pot reaction of aniline with triethyl orthoformate and sodium azide, was methylated with trimethyloxonium tetrafluoroborate [24] (Me_3OBF_4) to give pure **II** in 55% yield. The isolation and purification of **II** required a careful optimization involving reslurry with different solvents to avoid a column chromatography that would have led to the decomposition of the product. On the other hand, 2-phenyl-2*H*-tetrazole **III** [39] was obtained by diazotisation of aniline and subsequent reaction with formamidine hydrochloride. The methylation step was rather challenging, using MeI there is no product formation but the employment of Me_3OBF_4 as methylating agent gave **IV** in 83% yield.

The obtained tetrazolium salts were then used for the synthesis of the corresponding Ru complexes in a one-pot procedure (Scheme 1): the treatment of **II** and **IV** with Ag_2O gave the corresponding tetrazolylidenes which reacted in situ with the **Ru-dimer** to give **1** and **2** in 90% and 78% yield respectively. Complexes **1** and **2** are both air and moisture stable and can be purified by column chromatography on aluminium oxide.

The synthesis of **1** and **2** was followed by IR spectroscopy, observing a lowering in the CO stretching frequencies (e.g. **1**: ν(CO) = 2017, 1962 cm^{-1}; **2**: ν(CO) = 2014, 1955 cm^{-1} *vs.* **Ru-dimer**: 2018, 1967 cm^{-1}). Interestingly, by comparing IR spectra of **1** and **2** with those of imidazolylidene and triazolylidene complexes **3** and **4** (ν(CO) = 2004, 1945 cm^{-1}: identical for both complexes) a lower backbonding on terminal CO ligands is registered for tetrazolylidene complexes. Although not easy to rationalize, due to different geometric environment of the ligands, a lower σ-donor ability of tetrazolylidene could be taken into account, also evaluating the Ru-C distances from X-ray diffraction (*vide infra*).

Complexes **1** and **2** were further characterized by NMR and ESI-MS. ^{13}C NMR spectra show diagnostic signals at 175 ppm (**1**) and 182 (**2**) ppm for the Ru–C signals attributable to the carbene carbon, additionally molecular ions of complexes were detected by ESI-MS (see experimental).

Crystals suitable for single-crystal X-ray diffraction (SC-XRD) of ruthenium complex **2** were grown by slow diffusion of *n*-pentane into a saturated toluene solution of the complex. The bonding parameters are comparable to those previously found in related Ru complexes where the cyclopentadienone ligand was essentially η^4-coordinated [34,40,41]. Indeed, the Ru(1)-C(3) distance [2.4927(16) Å] is considerably elongated compared to Ru(1)-C(4) [2.2468(16) Å], Ru(1)-C(5) [2.2077(15) Å] Ru(1)-C(6) [2.1998(15) Å] and Ru(1)-C(7) [2.2686(15) Å]. Moreover, the C(3)-O(3) contact [1.2424(18) Å] is essentially a double bond. To the best of our knowledge, **2** represents the first Ru complex structurally characterized by SC-XRD that contains an mesoionic tetrazolylidene ligand, whereas a few examples have been reported for other metals [24,42,43]. The Ru(1)-C(41) bond distance [2.0903(16) Å] is similar to that found in related cyclopentadienone carbonyl Ru complexes containing NHC ligands [24,42,43]. The C(41)N(1)N(2)N(3)N(4) ring is perfectly planar [mean deviation from the least square plane 0.0008 Å] and the sum of the internal angles [541.0(3)°] is very close to that expected for a regular pentagon [540°] (Fig. 3).



Scheme 1. Synthesis of the methylated tetrazolylidene ligands (**II**–**IV**) and ruthenium complexes (**1** and **2**).

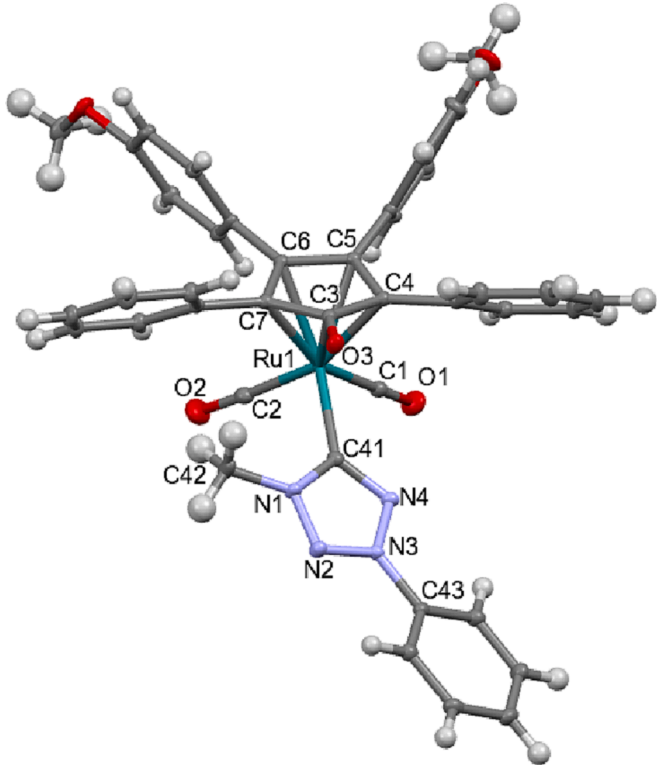


Fig. 3. Energy diagram ORTEP drawing of **2**. Displacement ellipsoids are at the 50% probability level. H-atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ru(1)-C(1) 1.8924(16), Ru(1)-C(2) 1.8860(17), Ru(1)-C(3) 2.4927(16), Ru(1)-C(4) 2.2468(16), Ru(1)-C(5) 2.2077(15), Ru(1)-C(6) 2.1998(15), Ru(1)-C(7) 2.2686(15), Ru(1)-C(41) 2.0903(16), C(1)-O(1) 1.142(2), C(2)-O(2) 1.146(2), C(3)-O(3) 1.2424(18), C(3)-C(4) 1.484(2), C(4)-C(5) 1.4470(19), C(5)-C(6) 1.428(2), C(6)-C(7) 1.4523(19, C(3)-C(7) 1.4785(19), C(41)-N(1) 1.3725(19), C(41)-N(4) 1.3431(19), N(1)-N(2) 1.3286(18), N(2)-N(3) 1.3029(18), N(3)-N(4) 1.3470(17), C(4)-C(3)-C(7) 104.31(12), C(3)-C(4)-C(5) 108.20(12), C(4)-C(5)-C(6) 108.61(12), C(5)-C(6)-C(7) 108.03(12), C(6)-C(7)-C(3) 108.64(12), N(1)-C(41)-N(4) 105.20(12), C(41)-N(1)-N(2) 112.55(12), N(1)-N(2)-N(3) 102.33(12), N(2)-N(3)-N(4) 115.00(12), N(3)-N(4)-C(41) 104.92(12).

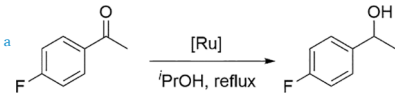
3.2. Reactivity of **1** and **2** in the catalytic transfer hydrogenation

Reactivity behaviour of ruthenium complexes **1** and **2** was investigated under transfer hydrogenation conditions, employing 4-fluoroacetophenone as model substrate and ^{i}PrOH as hydrogen source, following an already described procedure.[34] The principal aim was to compare the catalytic activity of complexes **1** and **2** with previously reported imidazolium **3** and triazolium **4** ruthenium complexes. In order to tune the role of *N*-heterocyclic carbene ligands with respect to their effect on stability of the carbonyl ligands, one of which is known to be removed for catalyst activation, [44] the reactions were conducted in ^{i}PrOH at reflux temperature. Samples were taken after 8 h and 24 h. Since both the reactant and the product have a fluorine atom, the conversions can be easily determined by ^{19}F NMR spectroscopy.

The obtained results (Table 1) show that tetrazolylidene ligands can indeed promote the activation of the pre-catalyst in refluxing 2-propanol (entry 3 and 4), conditions under which complexes **3** and **4**, with imidazolylidene or triazolylidene ligands, did not present any catalytic activity (entries 1 and 2). [34,35].

Quite surprisingly, while complex **2** converts 4-fluoroacetophenone with a modest 58% yield (entry 4),[44,45] complex **1** reached a complete conversion after 8 h (entry 3). Although both the results are likely to indicate a role of the tetrazolylidene ligand in ruthenium cyclopentadienone complexes activation, the hugely different behaviours

Table 1
Catalytic transfer hydrogenation of 4-fluoroacetophenone.



	[Ru]	Conversion (%)	
		8 h	24 h
1	**3**	0	0
2	**4**	0	0
3	**1**	100[b]	/
4	**2**	20	58
5[c]	**2**	0	6

[a] General condition: ruthenium complex (5 mol%), 4-fluoroacetophenone (0.3 mmol), ^{i}PrOH (3 mL), reflux; conversions determined by ^{19}F NMR spectroscopy.
[b] due to the degradation of ligand **II**, for clarification see text below. [c] experiment performed with 2-propanol-d_8.

open a question to the real destiny of the pre-catalyst after activation. Analysing the resting states of both the reactions shed light on the fact that complex **2** (the less active) is still the only species detectable after hydrogen transfer reaction, while complex **1** completely disappeared.

This behaviour agrees, in the case of **2**, with the previously demonstrated role of a pyridine substituent in lowering the energy needed for the CO release, while employing similar imidazolylidene based pre-catalysts.[44] In the latter case, the nitrogen in the substituent was found to be responsible for the pre-catalyst activation in refluxing ^{i}PrOH, and this can be the case also for the nitrogen containing tetrazolylidene in pre-catalyst **2**. It is also important to underline that the only presence of the pre-catalyst species **2** in the reaction crude, could be justified with the stabilization of the active catalyst in its precursor **2** at the end of the reaction exploiting the CO available in the reaction mixture.

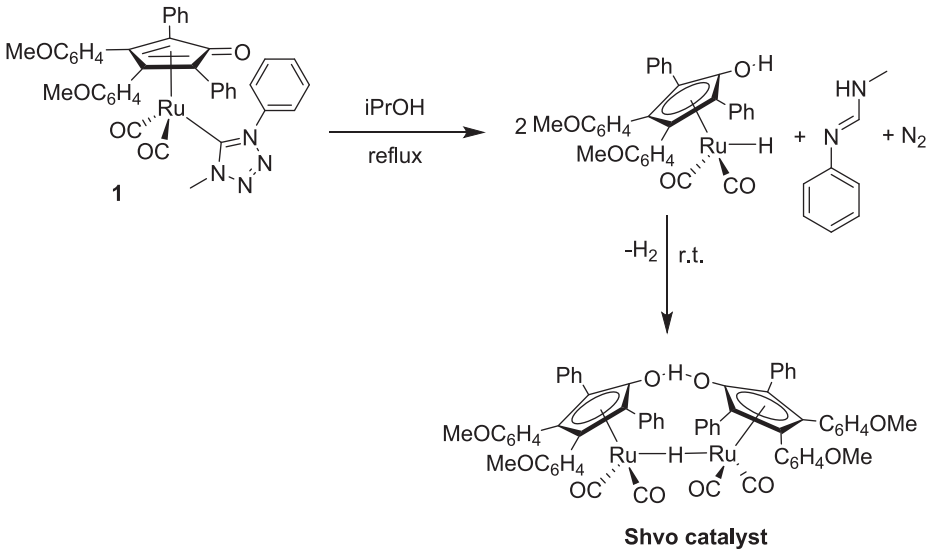
On the other hand, the spectroscopic characterization of the crude at the end of the catalytic test of entry 3, displayed different species both at NMR and IR spectra as compared to the precursor **1**. The crude was completely soluble and characterizations stated the presence of ruthenium carbonyl terminal ligands, a cyclopentadienone moiety and a bridging hydride with a negative chemical shifts. In particular, in ^{1}H NMR spectrum, we found the presence of a peak at −18 ppm (see supporting Fig. S15), while in IR spectrum bands from **1** were replaced by a peculiar set of bands at (2036, 2006, 1977 cm^{-1}).

Both the spectra are superimposable to that of a complex, largely employed by the group,[30,31,46] and well known in the literature as transfer hydrogenation catalyst, the stable dinuclear Shvo catalyst precursor,[28,29,47] which is likely the only one ruthenium based species in the resting state (Scheme 2). The result was also confirmed by ESI-MS were the molecular ion was detected at 1907 *m/z*.

This finding can be ascribed to the detachment of the tetrazolylidene ligand in the case of pre-catalyst **1**, which have the phenyl substituent in N4 position. Indeed under the reaction conditions, tetrazolylidene with unsubstituted nitrogen (N2 and N3) are prone to decompose releasing molecular nitrogen, as previously reported for similar heterocycles.[24].

That finally means that the real catalyst is the active form of Shvo precursor, making this result not interesting from a mere catalytic perspective, but useful from a reactivity point of view. Indeed performing the reaction in the absence of 4-fluoroacetophenone lead to the same result, pointing out that N4 substituted tetrazolylidene are thermally unstable. On the other hand, despite the low conversion, N3 substituted tetrazolylidene is found to be thermally stable under refluxing 2-propanol conditions and able, unlike what observed for imidazolylidene **3** and triazolylidene **4** complexes to promote hydrogen transfer reaction.

Lastly, with the aim of further investigating the reaction mechanism, a reaction test was carried out using deuterated 2-propanol-d_8. As shown



Scheme 2. Thermal decomposition of complex **1**.

in Table 1, entry 5, the conversion decreases up to 10 times. This shows that the source of hydrogen plays a non-innocent role and demonstrates that hydrogenation is the determining step of the reaction, and that the mechanism consists in a concerted proton and hydride transfer as previously reported for similar catalysts.[48].

The described behavior confirms the possibility to tune the pre-catalyst activation by varying the geometry, the steric encumbrance and the σ donor ability of the *N*-heterocyclic carbene toward an easier activation due to CO releasing and pave the way for the design of stable and tunable Ru(0) cyclopentadienone tetrazolylidene complexes for application in homogeneous catalysis.

4. Conclusions

We have synthesized two tetrazolium salts **II** and **IV**, and successively employed as pre-ligands to prepare the novel neutrals *N*-heterocyclic ruthenium complexes **1** and **2**. Complete characterization has been performed for each synthesized compound.

The reactivity of ruthenium complexes **1** and **2** investigated employing the complexes as pre-catalysts in the transfer hydrogenation reaction of the model substrate 4-fluoroacetophenone has been evaluated. While complex **1** (bearing a N4 substituted tetrazolylidene ligand) is thermally unstable due to detachment of the tetrazolylidene ligand, complex **2** (decorated with a N3 substituted tetrazolylidene ligand) shows a conversion, albeit low, higher than the imidazolylidene **3** and **4** triazolylidene congeners which are inactive.

The substituent position on tetrazolylidene ligands thus divides N3 and N4 substituted derivatives in term of stability. More in general, the new ruthenium tetrazolylidene complexes, especially the more stable N3 substituted, represent a step forward in the development of more stable and active *N*-heterocyclic carbene complexes, enlarging the possibilities for the fine tuning of steric and electronic properties toward catalytic applications.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary data

CCDC 2178977 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_ request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033. Supplementary data to this article can be found online at https://doi.org/10.1016/j.ica.2023.121472.

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