New insight into a deceptively simple reaction: the coordination of bpy to Ru(II)-carbonyl precursors. The central role of the *fac*-$[Ru(bpy)Cl(CO)_3]^+$ intermediate and the *chloride-rebound* mechanism.

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Abstract: This work demonstrates how a careful reexamination of well-trodden fields can fill conceptual gaps that previously escaped full understanding. The coordination of 2,2'-bipyridine (bpy) to the known Ru(II)-chlorido-carbonyl precursors – the dinuclear $[RuCl_2(CO)_3]_2$ (**P1**) and the polymeric $[RuCl_2(CO)_2]_n$ (**P2**) – has been investigated by several groups in the past, and a remarkably large number of ruthenium mono(bpy) carbonyls were identified and fully characterized. Many were investigated as catalysts or key intermediates for the photochemical, electrochemical, and photo-electrochemical reduction of CO_2, and for the water–gas shift reaction. Nevertheless, even though most – if not all – the reaction products are known already, a careful exam of the literature led us to believe that a convincing general scheme interconnecting them all was still missing and important questions remained unanswered. For this reason, we investigated the reactivity of two mononuclear Ru(II)-carbonyl-dmso precursors, *trans,cis,cis*-$[RuCl_2(CO)_2(dmso\text{-}O)_2]$ (**P3**) and *fac*-$[RuCl_2(CO)_3(dmso\text{-}O)]$ (**P4**) – that can be considered as 'activated forms' of **P2** and **P1**, respectively – towards the coordination of bpy. Compounds **P3** and **P4**, allowed us to gain new mechanistic insight and a deeper level of understanding. In particular, we found that coordination of bpy to **P4** (or **P1**) generates first the tricarbonyl cation *fac*-$[Ru(bpy)Cl(CO)_3]^+$.This key intermediate undergoes the facile and selective nucleophilic attack on the CO *trans* to Cl (by RO^- in alcoholic solvents or OH^- from adventitious water in other solvents), leading to all other species. We also demonstrated that Cl^- – even when in large excess – is unable to replace a carbonyl on *fac*-$[Ru(bpy)Cl(CO)_3]^+$. However, the chloride set free from the precursor, competes efficiently with bpy for the coordination to Ru(II) (*chloride rebound* mechanism).

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Supporting information for this article is given via a link at the end of the document. CCDC 1403125-1403129 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

1. Introduction

Ruthenium(II) carbonyl compounds with one or two diimine chelating ligands (*N*-*N*), such as $[Ru(bpy)Cl_2(CO)_2]$ and $[Ru(bpy)_2(CO)(X)]^{n+}$ (bpy = 2,2'-bipyridine, X = Cl, CO, CO_2, C(O)OH, CHO, CH_2OH, and CH_3; n = 1, 2 depending on X), have been extensively investigated as catalysts or key intermediates for the photochemical, electrochemical, and photo-electrochemical reduction of CO_2,[1-9] and for the water–gas shift reaction.[10-13] These compounds were tested also as catalysts in the hydroformylation of 1-hexene and hydrogenation of 1-heptanal,[14,15] and in hydrogen transfer reactions.[16] In addition, dicarbonyl complexes of the type $[Ru(bpy)Cl_2(CO)_2]$ are excellent precursors to heteroleptic bis- and tris-(diimine)ruthenium(II) complexes. These latter, by virtue of their photoluminescent and redox properties,[17] are – in turn – extensively investigated as photosensitizers for the conversion of solar light into chemical or electrical energy,[18] as photo-redox catalysts for water splitting,[19,20] as well as electro-chemiluminescent molecular probes for biosensing and biomedical applications.[21-23]

This paper is focused on the preparation of the Ru(II) diimine carbonyl compounds and on the complex network of chemical pathways interconnecting many of them, which is obviously relevant towards understanding the catalytic processes of these species. For the sake of simplicity, a single diimine – bpy – will be considered, since a large amount of data is available for complexes with this ligand.

We are particularly interested in the first synthetic step, i.e. the coordination of bpy to the Ru(II)-chlorido-carbonyl precursors with formation of ruthenium mono(bipyridine) carbonyls. Despite the apparent simplicity of this reaction, it can generate a remarkably large number of products, depending on the reaction conditions (solvent, ligand/Ru ratio, temperature). In this paper we first review the main synthetic approaches from the most widely used Ru(II)-carbonyl precursors whereas, in the second part, we compare the literature data with ours, obtained using as precursors two mononuclear Ru(II)-carbonyl-dmso compounds previously developed by us.[24] We believe that the critical review of the literature data combined with our results provides a significant deeper insight into this highly relevant topic.

A considerable problem in the field of ruthenium mono(bipyridine) carbonyls is that of distinguishing unambiguously among the many similar products – including stereoisomers – that can be formed. Since each product complex has at least two carbonyls, and CO stretching frequencies in the solid state are affected by experimental

parameters, IR spectra are not suitable to this purpose, in particular when one considers that these compounds are often isolated as mixtures. Indeed, the early literature in this field, that relied heavily on IR data and on the color of the complexes in the solid state, is quite confusing and largely unreliable. Basically, only ^{1}H NMR spectroscopy can rapidly and unambiguously determine the nature of the species under investigation, also when produced as mixtures and in small amounts. However, since very often ^{1}H NMR spectroscopy can count only on the bpy resonances to distinguish among similar species, and we noticed that for each species some chemical shifts of bpy protons can be remarkably affected by the nature of the solvent, a comprehensive proton NMR database of the main species – that will allow the unambiguous recognition of each compound – is also provided here (Table 1 and Experimental Section). The ^{13}C NMR resonances of the carbonyl ligands in these species, most of which are also available from the literature (Table 2), are a useful complement to the proton NMR data for determining their stoichiometry and geometry.

2. Literature survey

2.1. Ru(II) carbonyl precursors P1 and P2

There are basically two Ru(II)-chlorido-carbonyl precursors that are widely used for synthetic purposes: the dinuclear species $[RuCl_2(CO)_3]_2$ (**P1**), that features two {*fac*-$RuCl(CO)_3$} fragments held together by two bridging chlorides, and the less well characterized polymeric species $[RuCl_2(CO)_2]_n$ (**P2**), in which each unit is believed to feature two adjacent carbonyls and four bridging chlorides (Figure 1). Both **P1** and **P2** can be obtained in a single step and good yields from hydrated $RuCl_3$, the universal ruthenium precursor. The poorly characterized "*red carbonyl solution*", obtained by reaction of carbon monoxide with hydrated $RuCl_3$ in refluxing ethanol and also used in earlier reports,[25-27] proved to be a scarcely reproducible precursor and was later abandoned. For this reason, it will not be dealt with here.

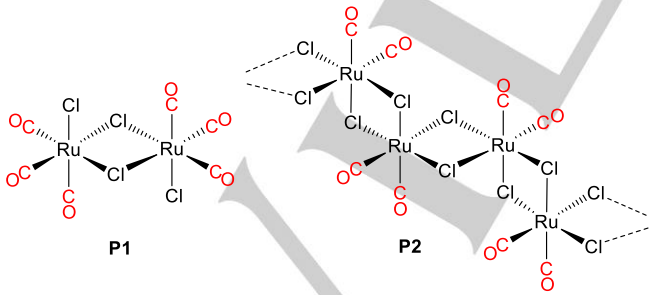
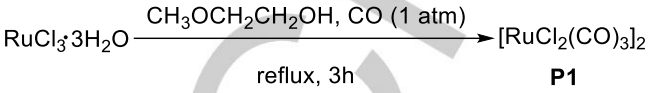


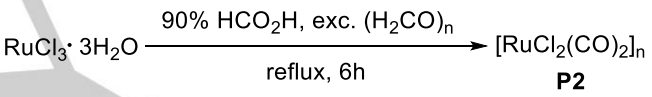
Figure 1. Schematic structures of the two commonly used Ru(II)-chlorido-carbonyl precursors, the dimer $[RuCl_2(CO)_3]_2$ (**P1**) and the polymer $[RuCl_2(CO)_2]_n$ (**P2**).

Following the original report by Bruce and Stone in 1967,[28] several synthetic procedures have been reported for the preparation of **P1**, some of them using $Ru_3(CO)_{12}$ as precursor.[29] The most recent and efficient procedure requires the treatment of $RuCl_3{\cdot}nH_2O$ with CO in refluxing 2-methoxyethanol (Scheme 1).[30] Evaporation of the solvent affords **P1** as an off-white to slightly yellow solid. This precursor is also commercially available.



Scheme 1. Preparation of $[RuCl_2(CO)_3]_2$ (**P1**).[30]

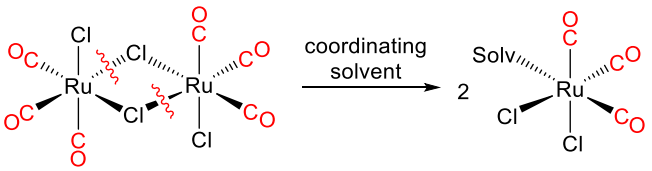
Polymer **P2** is obtained by treating $RuCl_3{\cdot}nH_2O$ either with CO in refluxing ethanol or – preferably – with an excess of paraformaldehyde in a refluxing solution of 90% formic acid (Scheme 2).[31-33] Evaporation of the solution to dryness affords **P2**, often contaminated by small amounts of the dimer **P1**, as a pale yellow powder. In many cases the polymeric precursor **P2** is not isolated as a solid, but prepared in solution and treated *in situ* with the appropriate ligand.



Scheme 2. Preparation of $[RuCl_2(CO)_2]_n$ (**P2**).[32,33]

2.2. Reactivity of P1 with bpy

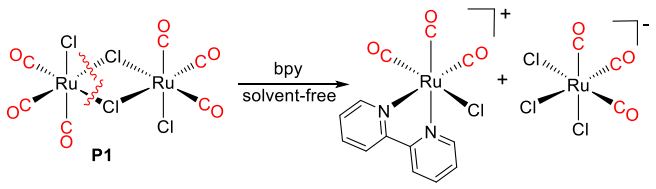
The reactivity of dimer **P1** towards chelating diimine ligands (*N*-*N*) has been investigated by several groups: outstanding contributions have been provided, in particular, by the group of Pakkanen.[15,34,35] The typical reactivity of **P1** involves fragmentation of the dimer into monomeric species, either in a symmetrical or unsymmetrical fashion, depending on the conditions (solvent and temperature) and the nature of the incoming ligand. In coordinating solvents the dimer is cleaved symmetrically (Scheme 3), generating two equal neutral {*fac*-$RuCl_2(CO)_3$} fragments. The solvent derivatives *fac*-$[RuCl_2(CO)_3(Solv)]$, with Solv = CH_3CN and THF, have been isolated and fully characterized.[15,36,37] We prepared the corresponding dimethylsulfoxide complex, *fac*-$[RuCl_2(CO)_3(dmso\text{-}O)]$, by a completely different route (see below).[24]



Scheme 3. Typical reactivity of $[RuCl_2(CO)_3]_2$ (**P1**) in coordinating solvents.[15]

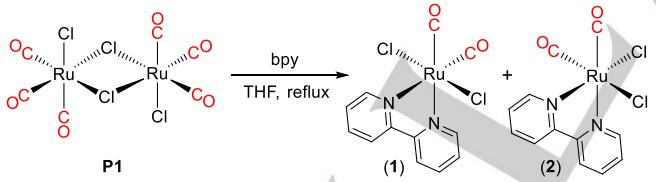
The molecule of coordinated solvent is then easily and selectively replaced by aromatic nitrogen ligands, such as pyridine, pyrazine and thiazole.[15,37-39]

It should be noted that when the unsymmetrical fragmentation of the dimer **P1** occurs (such as – apparently – when the reaction with bpy was performed in dry 'solvent-free' conditions),[15] the *fac*-$[RuCl_3(CO)_3]^-$ anion is generated together with the Ru(II) cationic fragment *fac*-$[Ru(bpy)Cl(CO)_3]^+$, thus wasting half of the ruthenium amount (Scheme 4).



Scheme 4. Asymmetrical fragmentation of $[RuCl_2(CO)_3]_2$ (**P1**) in the solvent-free reaction with bpy.

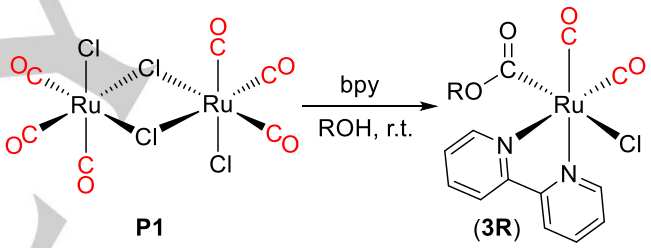
The reactivity of **P1** towards bpy – and towards chelating diimines in general – depends strongly on the solvent, on the temperature, and on the bpy/Ru ratio. According to Pakkanen and coworkers,[34] treatment of **P1** with a twofold excess of bpy in refluxing THF leads to a mixture of the two neutral mono-bpy isomers *trans,cis*- and *cis,cis*-$[Ru(bpy)Cl_2(CO)_2]$ (**1** and **2**, respectively; Scheme 5). Thus, bpy formally replaces the coordinated solvent and one carbonyl in the *fac*-$[RuCl_2(CO)_3(thf)]$ intermediate obtained from **P1** in these conditions (see above).



Scheme 5. Reactivity of $[RuCl_2(CO)_3]_2$ (**P1**) towards bpy in refluxing THF.[34]

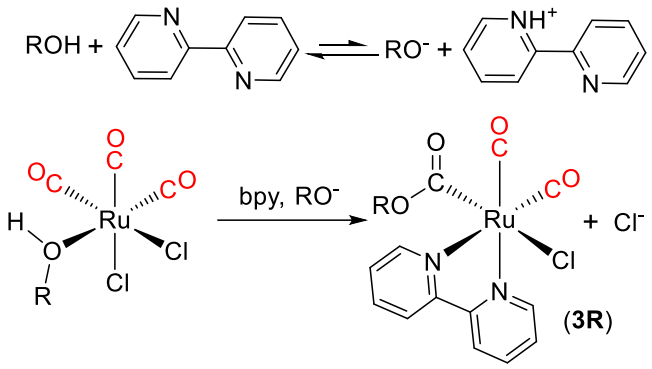
The two yellow isomers were separated by crystallization and characterized individually, including the X-ray structure. They are easily and unambiguously distinguished by ^1H NMR spectroscopy: The spectrum of **1** shows four aromatic resonances, typical of bpy coordinated in a symmetrical environment, whereas that of **2** shows eight bpy resonances (the two pyridyl rings are inequivalent, being one *trans* to CO and the other *trans* to Cl). Each isomer is stable in solution and shows no tendency to convert spontaneously to the other, thus suggesting the existence of a high energy transition state between the two.[40] From the literature data it is unclear which of the two isomers is thermodynamically more stable. According to DFT calculations isomer **1** is more stable than **2** by only +0.4 kJ/mol.[40,41] The third possible stereoisomer, *cis,trans*-$[Ru(bpy)Cl_2(CO)_2]$, that presumably is thermodynamically disfavored by the π-back bonding competition of the two *trans* carbonyls, has never been isolated. Its energy has been calculated to be +44.6 kJ/mol higher than that of **1**.

Conversely, the same group of Pakkanen found that treatment of dimer **P1** with an excess of bpy in refluxing methanol led to the isolation of the pale yellow methoxycarbonyl complex *trans,cis*-$[Ru(bpy)Cl(C(O)OCH_3)(CO)_2]$ (**3Me**).[34] On the other hand, when the reaction was performed in higher boiling alcohols (e.g. ethanol, 2-propanol) only mixtures of **1** and **2** were obtained.[34] In subsequent papers, the same group reported that, in general, treatment of **P1** with bpy in an alcohol (e.g. methanol or ethanol) or ethylene glycol affords the corresponding alkoxycarbonyl product of the general formula *trans,cis*-$[Ru(bpy)Cl(C(O)OR)(CO)_2]$ (**3R**) (Scheme 6, R = CH_3, CH_2CH_3, CH_2CH_2OH) even at room temperature.[15,40,42] The pale-yellow complexes have been fully characterized spectroscopically and their X-ray structures also determined.[15,34,40]



Scheme 6. Reactivity of $[RuCl_2(CO)_3]_2$ (**P1**) towards bpy in alcoholic solvents with formation of the alkoxycarbonyl compound **3R**.[15,40]

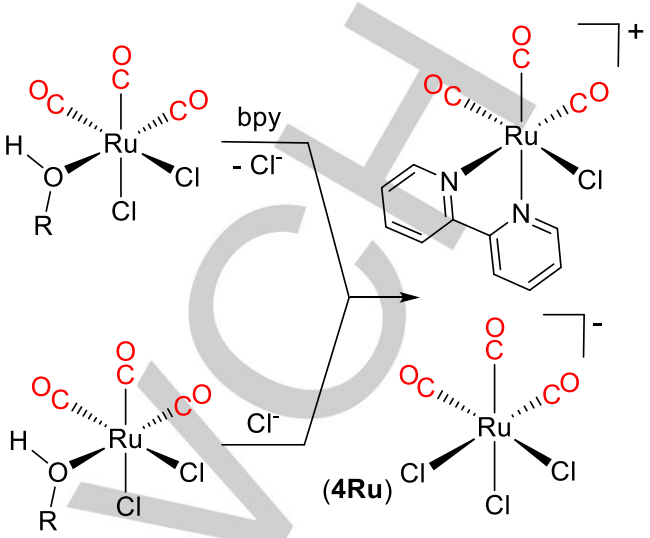
In all cases, the alkoxycarbonyl moiety is always *trans* to the chloride. From the mechanistic point of view, formation of compound **3R** involves the presence of alkoxy ions in solution. It is believed that the bpy ligand (in excess) acts as a weak base, deprotonating the alcohol solvent and generating alkoxy ions that are able to perform a nucleophilic attack onto a carbonyl carbon of the tricarbonyl mononuclear intermediate *fac*-$[RuCl_2(CO)_3(ROH)]$ that is generated by the fragmentation of **P1** (Scheme 7).



Scheme 7. Suggested mechanism for the formation of the alkoxycarbonyl products **3R** from **P1** in alcoholic solvents.

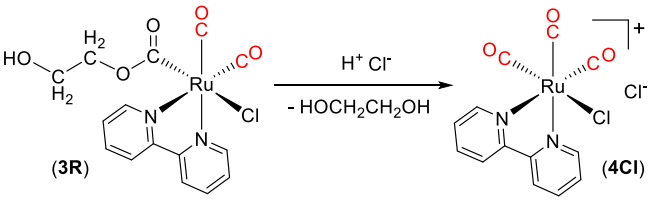
From the above reaction scheme proposed by Pakkanen and coworkers,[15] it is however unclear if coordination of bpy occurs prior to the nucleophilic attack of the alkoxy ion or afterwards, and why this specific geometry, with the two anionic ligands *trans* to each other, is selectively obtained. Typically alkoxycarbonyl ruthenium complexes are prepared by treatment of carbonyl derivatives with strong bases such as sodium or potassium methoxide.[43]

From the reaction between **P1** and bpy in alcoholic media a sub-product was also isolated: the almost colorless to pale-pink ion-pair complex *fac*-$[Ru(bpy)Cl(CO)_3]^+$*fac*-$[RuCl_3(CO)_3]^-$ (**4Ru**), whose relative amount was found to increase upon decreasing the bpy/Ru ratio.[15] Indeed, whereas compound **3** is largely predominant when an excess of bpy is used, when bpy/Ru = 0.5 complex **4Ru** was the only reaction product isolated. The mechanism proposed for the formation of **4Ru** in alcohols, that might be seen formally as the result of an asymmetric fragmentation of **P1** (see above Scheme 4) is illustrated in Scheme 8. The cationic fragment is believed to be the consequence of the direct attack of bpy on the neutral intermediate, replacing the alcohol ligand and a chloride. Upon decreasing the amount of free bpy base, the formation of alkoxy ions at equilibrium becomes negligible and therefore the liberated chloride ion attacks the intermediate, replacing the alcohol ligand and producing the anionic fragment.



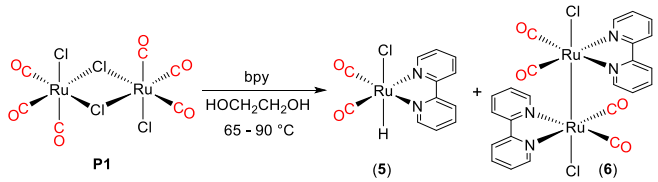
Scheme 8. Suggested mechanism for the formation of the ion-pair complex product **4Ru** from **P1** in alcoholic solvents.[15]

Notably, the chloride salt of the tricarbonyl complex cation, i.e. *fac*-$[Ru(bpy)Cl(CO)_3]Cl$ (**4Cl**, characterized also through the X-ray structure), was obtained by treatment of the solid, nearly white glycoxycarbonyl complex *trans,cis*-$[Ru(bpy)Cl(C(O)OCH_2CH_2OH)(CO)_2]$ with concentrated HCl at room temperature (Scheme 9).[40] This process can be seen as the reverse reaction of the nucleophilic attack of glycolate on the tricarbonyl intermediate *fac*-$[RuCl_2(CO)_3(ROH)]$ (or rather on *fac*-$[Ru(bpy)Cl(CO)_3]^+$), with H^+ attacking the esteric oxygen atom. It also suggests that Cl^- (even if in large excess) is unable to replace a CO ligand on *fac*-$[Ru(bpy)Cl(CO)_3]^+$ under mild conditions. Conversely, when *trans,cis*-$[Ru(bpy)Cl(C(O)OCH_2CH_2OH)(CO)_2]$ was treated with a small amount of concentrated HCl in ethylene glycol at 100 °C a mixture of isomers **1** and **2** was obtained.[40] Pakkanen and co-workers suggested that *fac*-$[Ru(bpy)Cl(CO)_3]^+$ is an intermediate in the formation of **1** and **2**, with Cl^- replacing directly one of the carbonyls. This important mechanistic step – on which we disagree – will be discussed in more detail below.



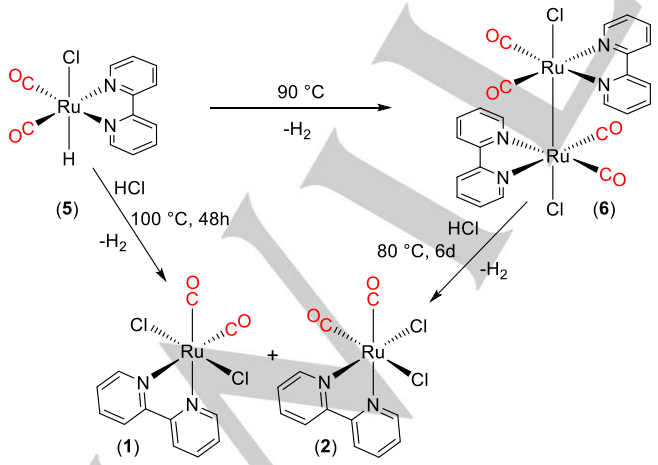
Scheme 9. Formation of *fac*-$[Ru(bpy)Cl(CO)_3]Cl$ (**4Cl**) upon treatment of solid *trans,cis*-$[Ru(bpy)Cl(C(O)OCH_2CH_2OH)(CO)_2]$ (**3R**) with concentrated HCl.[40]

When the reaction between **P1** and an excess of bpy in ethylene glycol was performed at 65 – 100 °C rather than at room temperature, the intermediate species *trans,cis*-[Ru(bpy)Cl(C(O)OCH$_2$CH$_2$OH)(CO)$_2$] was found to react further and two new main neutral products were isolated and characterized: the orange-brown monomeric hydrido complex *trans,cis*-[Ru(bpy)ClH(CO)$_2$] (**5**) and the very insoluble orange-red Ru(I) dimer [*cis*-Ru(bpy)Cl(CO)$_2$]$_2$ (**6**), characterized by a Ru–Ru bond (Scheme 10).[15,34,40] In addition, the dichlorido isomers **1** and **2** were isolated as side products of the reaction. The monomer **5** is formed first (and only when the solvent contains adventitious water), and is converted into the dimer upon increasing the reaction time and/or the reaction temperature. The dimeric species **6** has the chlorides in apical positions and crystallizes as a mixture of staggered and anti-eclipsed rotamers.[34]



Scheme 10. Reactivity of **P1** towards bpy in hot ethylene glycol with formation of *trans,cis*-[Ru(bpy)ClH(CO)$_2$] (**5**) and [*cis*-Ru(bpy)Cl(CO)$_2$]$_2$ (**6**).[15,34,40]

It was also demonstrated that heating monomer **5** in ethylene glycol or toluene at 90 °C leads to the precipitation of **6**, accompanied by evolution of H_2 (Scheme 11).[34] In addition, the treatment of both species **5** and **6** in ethylene glycol containing a small amount of 37% HCl leads to the evolution of H_2 and to the formation of the dichlorido complexes **1** and **2**, whose relative amounts depend on the reaction conditions. For example, prolonged heating at 100 °C of **5** under the above conditions led to almost pure **2** in very high yield (implying isomerization).

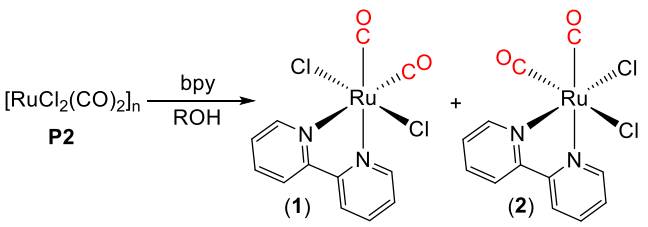


Scheme 11. Network of reactions interconnecting species **1**, **2**, **5** and **6**.

Finally, precursor **P1** – besides substitution reactions – can undergo also nucleophilic attack on the carbonyls. Noteworthy, Lavigne and co-workers found that – in the absence of any chelating diimine – treatment of a solution of *fac*-[RuCl$_2$(CO)$_3$(thf)] in 2-methoxyethanol with one equivalent of KOH (1M in methanol) at 25 °C led to the instantaneous quantitative formation of the hydroxycarbonyl compound [Ru(CO)$_2$Cl$_2$(C(O)OH})]$^-$.[30] Decarboxylation of this species at 85 °C under a CO stream led, presumably through the elusive hydrido intermediate [Ru(CO)$_2$Cl$_2$H]$^-$, to the almost quantitative formation of the Ru(0) cluster Ru$_3$(CO)$_{12}$.[30]

2.3. Reactivity of P2 with bpy

As originally reported by Thomas and co-workers,[44] and later implemented and exhaustively reviewed by Spiccia and co-workers,[33] when the polymeric precursor [RuCl$_2$(CO)$_2$]$_n$ (**P2**) is treated with bpy in refluxing methanol (or, in general, in an alcoholic solvent) it readily affords in high yield the neutral Ru(II) complex *trans,cis*-[Ru(bpy)Cl$_2$(CO)$_2$] (**1**). The preparation can be generalized to include other chelating diimines as well. A later report by Deronzier, Ziessel and co-workers,[7] described the selective preparation of either **1** or its isomer *cis,cis*-[Ru(bpy)Cl$_2$(CO)$_2$] (**2**) by treatment of **P2** with bpy in methanol at room temperature: selectivity depends – for unclear reasons – on the conditions used for preparation of the polymeric precursor and on the pH of the reaction mixture. Thus, the reactivity of [RuCl$_2$(CO)$_2$]$_n$ towards bpy (Scheme 12) is overall much simpler than that established for **P1**, and basically involves the fragmentation of the polymer into the monomeric component, followed by coordination of the diimine. Depending on the conditions, isomerization of the two chlorides from *trans* to *cis* can occur. No other compound – and notably no alkoxycarbonyl product – was isolated.[45] This finding implies that the carbonyls in **P2** are much less electrophilic compared to those in **P1**. Also this issue will be discussed in detail below.

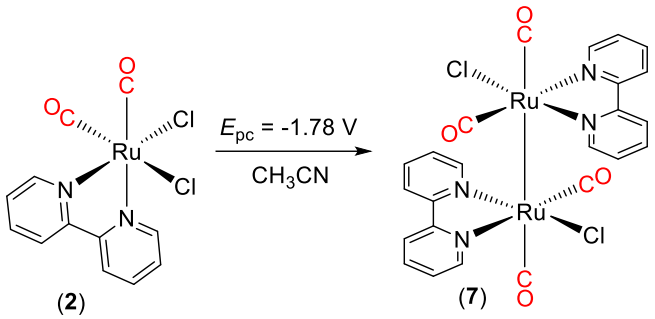


Scheme 12. Reactivity of [RuCl$_2$(CO)$_2$]$_n$ (**P2**) towards bpy in refluxing alcohols.[7, 33]

Being composed of chlorido-bridged dicarbonyl monomeric units, **P2** is obviously unsuited as precursor for the preparation of tricarbonyl derivatives and this is most likely the reason for its simpler reactivity compared to **P1** (see below). In addition, given that the nature of polymeric **P2** remains rather undefined, and considering that often it is not isolated as a solid but generated from hydrated RuCl$_3$ and used as such in solution, the precise

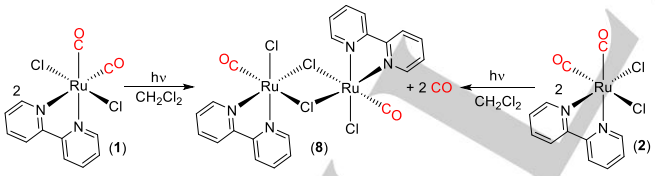
control of the stoichiometry of its substitution reactions is a difficult task.

The same groups that investigated the coordination of bpy to **P2** have also studied the subsequent reactivity of the isomeric products **1** and **2**. It was found by Ziessel and co-workers that the electrolysis of **1** leads to the polymer $[Ru(bpy)(CO)_2]_n$ – that contains Ru^0–Ru^0 bonds – through the intermediate formation of the dinuclear Ru(I)–Ru(I) species **6** (see above), whereas the exhaustive one-electron reduction of **2** leads only to an isomer of dimer **6**, i.e. compound **7** with apical CO – rather than Cl – ligands, and no further reduction was observed (Scheme 13).[7,46]



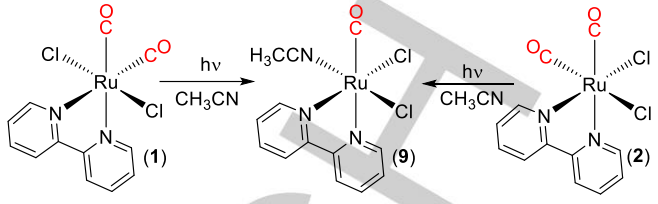
Scheme 13. One-electron reduction of **2** leading to the dinuclear Ru(I)–Ru(I) species **7** (an isomer of **6**).[7]

Spiccia and co-workers first established that light is an important factor in the reactivity of $[Ru(N\text{–}N)(CO)_2Cl_2]$ complexes, where *N*–*N* = bpy or a related diimine. They found that irradiation of **1** with white light in poorly coordinating solvents (such as DCM) induces mono-decarbonylation with subsequent formation of the insoluble dinuclear complex with two bridging chlorides $[Ru(bpy)Cl(CO)(\mu\text{-}Cl)]_2$ (**8**) (Scheme 14).[47]



Scheme 14. Photo-induced decarbonylation of **1** and **2** in non-coordinating solvents leading to the dinuclear complex $[Ru(bpy)Cl(CO)(\mu\text{-}Cl)]_2$ (**8**).[47]

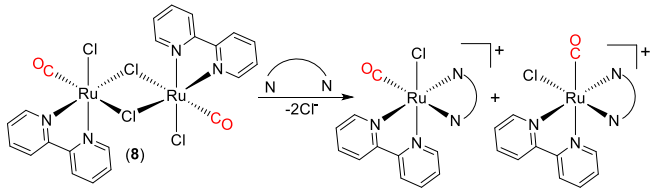
Later, Haukka and co-workers found that the same dimer **8** is obtained also from **2** under similar conditions (Scheme 14), whereas (confirming an earlier report by other authors[48]) photo-irradiation at 366 nm of both **1** and **2** in coordinating CH_3CN leads within ca. 1h to the same mono-acetonitrile complex *cis,cis*-$[Ru(bpy)Cl_2(CO)(CH_3CN)]$ (**9**, Scheme 15).[49] Similar results (i.e. decarbonylation and solvent coordination) were found also when photoirradiation of **1** with visible light was performed in methanol.[50]



Scheme 15. Photo-induced decarbonylation of **1** and **2** in the coordinating solvent acetonitrile leading to the mononuclear complex *cis,cis*-$[Ru(bpy)Cl_2(CO)(CH_3CN)]$ (**9**).[49]

In apparent contrast with what found in the above described synthetic procedures, that required prolonged irradiation times (minutes), Gabrielsson et al. reported that **1** undergoes ultrafast CO release in CH_3CN solution upon excitation with a laser at 400 nm.[51] Very recently, a series of Ru(II) dicarbonyl complexes with functionalized 2,2′-bipyridine and structurally similar to **1** were found to release one equiv of CO per mole of complex upon illumination at 365 nm in water/DMSO solution, thus qualifying as a new class of photoCORMs (photoinduced CO Release Molecules) for potential biomedical applications.[52]

As already mentioned, Spiccia and co-workers established two efficient synthetic pathways that exploit the neutral dicarbonyl derivatives **1** and **2** as convenient precursors in the preparation of heteroleptic tris-(diimine)ruthenium(II) complexes.[33] The first step concerns the preparation of heteroleptic bis-(diimine)ruthenium(II) intermediates. In the so-called *photodecarbonylation route* the reaction of **8** (obtained from **1** or **2** as reported above) with a chelating diimine *N-N* in refluxing 2-methoxyethanol results in cleavage of the dichlorido bridge and formation of cationic *cis*-$[Ru(bpy)(N\text{-}N)(CO)Cl]^+$ complexes (mixture of the two stereoisomers) (Scheme 16).[53]



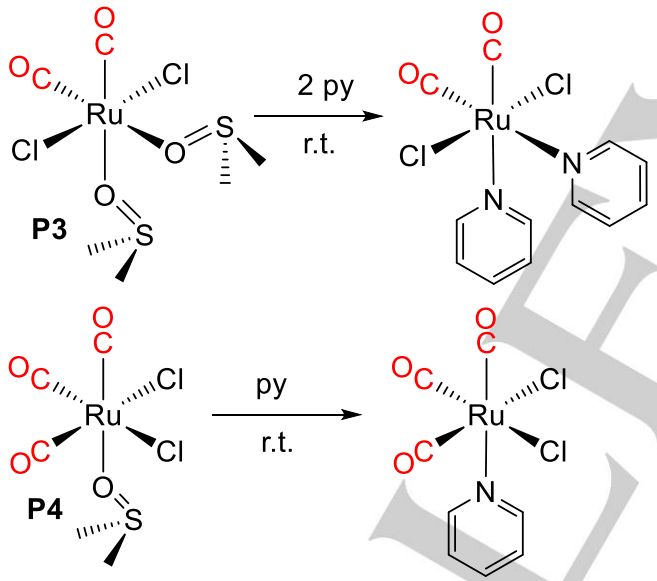
Scheme 16. Second step in the *photodecarbonylation route* to heteroleptic tris-(diimine)ruthenium(II) complexes.[33]

In the alternative, but less efficient, *triflate route*, dicarbonyl complexes of the type *cis*-$[Ru(bpy)(N\text{-}N)(CO)_2]^{2+}$ are instead prepared from **1** through the triflate intermediate *cis,cis*-$[Ru(bpy)(CO)_2(CF_3SO_3)_2]$.[33] In both routes, the final step requires reaction of the heteroleptic bis-(diimine)ruthenium(II) intermediates with a dissimilar diimine (*N′-N′*) in the presence of trimethylamine-N-oxide as decarbonylating agent.

2.4. Ru(II)-dmso di- and tricarbonyl precursors

In the past we have prepared and characterized a series of neutral Ru(II)-dmso carbonyl compounds featuring from one to three carbonyls.[24,54] The preparations involved the treatment of the two isomeric Ru(II)-dmso chlorido precursors *cis,fac*-[$RuCl_2$(dmso-O)(dmso-S)$_3$] and *trans*-[$RuCl_2$(dmso-S)$_4$] with carbon monoxide under different conditions. Coordination of CO always induced the selective S-to-O linkage isomerization of the dmso *trans* to it for avoiding π-back bonding competition. More recently we also described cationic mono- and di-carbonyl Ru(II)-dmso compounds.[55]

In this context, we focus on the two neutral complexes *trans,cis,cis*-[$RuCl_2(CO)_2$(dmso-O)$_2$] (**P3**) and *fac*-[$RuCl_2(CO)_3$(dmso-O)] (**P4**) that were proved already to be excellent precursors in inorganic synthesis, since the dmso-O ligand *trans* to a carbonyl can be selectively replaced by a neutral σ-donor N ligand (e.g. NH_3 or pyridine) under mild conditions, without affecting the rest of the coordination sphere. For example, when treated with a slight excess of pyridine at room temperature, **P3** and **P4** selectively afford the corresponding products *trans,cis,cis*-[$RuCl_2(CO)_2$(py)$_2$] and *fac*-[$RuCl_2(CO)_3$(py)] (Scheme 17).[24,56]



Scheme 17. Model reactions of the Ru(II)-dmso carbonyl precursors *trans,cis,cis*-[$RuCl_2(CO)_2$(dmso-O)$_2$] (**P3**) and *fac*-[$RuCl_2(CO)_3$(dmso-O)] (**P4**) towards pyridine.

In the metal-mediated approach to the construction of supramolecular assemblies, **P3** proved to be a very convenient precursor for the neutral 90°-angular linker fragment *trans,cis*-{$RuCl_2(CO)_2$}. Indeed, this compound has been extensively exploited by us for the construction of stable metallacycles of *meso*-pyridylporphyrins.[57]

Thus, when compared to the Ru(II)-carbonyl precursors **P1** and **P2** described above, **P3** can be considered as an 'activated' repetitive unit of polymer **P2**, with the two adjacent coordination sites occupied by labile dmso-O ligands. On the other hand, compound **P4** – even though prepared by carbonylation of *cis,fac*-[$RuCl_2$(dmso-O)(dmso-S)$_3$] – can be thought of as deriving from dimer **P1** upon symmetrical cleavage in DMSO. In other words it is an 'activated' form of **P1**.

At this stage, it is legitimate to ask what are the motivations for investigating the reactivity of **P3** and **P4** towards the coordination of bpy (as representative of a generic chelating diimine). What else can be learned in this already well-trodden field? The literature survey reported above demonstrates that, despite its apparent intrinsic simplicity, the coordination of bpy to the known Ru(II)-carbonyl precursors can generate a remarkably large number of products, most of which – if not all altogether – have been identified and fully characterized. Nevertheless, even though all the pieces (i.e. the reaction products) are on the chessboard already, the careful examination of the literature led us to believe that a convincing general scheme interconnecting them all is still missing and important questions still remain unanswered. In particular:

- What is the mechanism leading from the tricarbonyl precursor **P1** to the dicarbonyls **1** and **2** in refluxing THF?
- Is bpy capable of replacing *directly* one carbonyl from the {*fac*-$RuCl_2(CO)_3$} fragment or another mechanism takes place?
- Is chloride capable of replacing *directly* one carbonyl on the bpy derivatives of **P1**?
- When operating in alcoholic solvents (ROH), on which species does the nucleophilic attack of RO^- occur?

We reasoned that perhaps compounds **P3** and **P4** might have suitable characteristics for allowing us to get more insight into this deceptively simple system. In particular, the following advantages might derive from the use of **P3** and **P4**: *i*) In **P1** and **P2** the symmetrical or asymmetrical cleavage of the chloride bridges can – in principle – lead to different species. This problem is avoided with the mononuclear precursors **P3** and **P4**; *ii*) Compared to polymeric **P2**, mononuclear **P3** has the clear advantage of being a well characterized and exactly measurable compound; *iii*) Both **P3** and **P4** are soluble in several different solvents, ranging from water to chloroform and including acetone and alcohols. Given the relevance of the solvent in the reactivity of **P1** towards bpy, they might allow us to perform preparations in solvents that have not been investigated before (for example, **P1** is described as poorly soluble in chloroform); *iv*) Being **P3** and **P4** already 'activated' precursors, it should be possible to perform their reactions under milder conditions and thus to isolate, or at least detect, important – and otherwise elusive – intermediates.

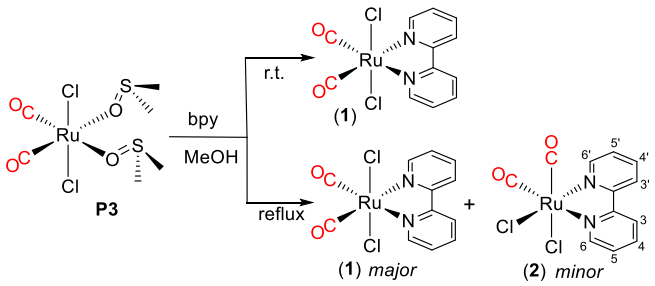
3. Results and discussion

All the synthetic procedures were performed in light-protected conditions, unless otherwise stated.

3.1. Treatment of *trans,cis,cis*-[$RuCl_2(CO)_2$(dmso-O)$_2$] (P3) with bpy

Consistent with its known substitution chemistry, we found that

treatment of **P3** with one equivalent of bpy in methanol at room temperature affords selectively *trans,cis*-[Ru(bpy)$Cl_2(CO)_2$] (**1**) in good isolated yield (Scheme 18). Formation of the corresponding *cis,cis*-[Ru(bpy)$Cl_2(CO)_2$] (**2**) isomer was not observed under these conditions. When the reaction was performed in refluxing methanol or ethanol, first a crop of pure isomer **1** precipitated spontaneously, whereas a small amount of a mixture of **1** and **2** (with **1** largely prevailing according to NMR spectra) was obtained from the mother liquor after concentration.



Scheme 18. Reactions of **P3** with bpy in MeOH (or EtOH).

An increase of the reflux time from 2 to 4 h and of the bpy:**P3** ratio from 1 to 2 induced no significant difference. As already mentioned, the ^{1}H NMR spectrum of **1** shows four equally intense multiplets, as expected for the two equivalent pyridyl rings of bpy, whereas the less symmetrical **2** has eight bpy resonances. In the spectrum of **2**, the two doublets of H6 and H6' have a large $\Delta\delta$, falling ca. 1 ppm apart (in $CDCl_3$). The most downfield resonance can be safely attributed to H6, i.e. the proton that points towards the adjacent chloride (i.e. that on the pyridyl ring trans to CO, see Scheme 18), as already observed in other Ru(II) complexes in which protons with a partial positive charge (such as those adjacent to the pyridyl nitrogens in bpy) are close in space to coordinated halides.[58] Interestingly, the HSQC spectra showed that the ^{13}C NMR resonances of C6 and C6' are quite sensitive to the geometry of the complex (whereas those of all other bpy carbons are not): In acetone-d_6 the C6/6' resonance of **1** (153 ppm) falls basically in between those of C6 (149 ppm) and C6' (156 ppm) of **2**. Finally, it should be noted that the proton chemical shifts of both **1** and **2** are significantly affected by the nature of the solvent (Table 1 and Experimental Section). For the carbonyl resonances, see Table 2.

Table 1. ^{1}H NMR chemical shifts (ppm) and coupling constants *J* (Hz) of the bpy protons in the Ru(II)-carbonyl compounds in which bpy is coordinated in a symmetrical environment. Each resonance integrates for 2H.

	Solvent	H6,6'	H5,5'	H4,4'	H3,3'
1	$CDCl_3$	9.21 (dd, *J* = 5.4, 0.7 Hz)	7.68 (ddd, *J* = 7.5, 5.5, 1.3 Hz)	8.13 (td, *J* = 7.9, 1.5 Hz)	8.24 (d, *J* = 8.1 Hz)
1	$(CD_3)_2CO$	9.28 (ddd, *J* = 5.4, 1.5, 0.7 Hz)	7.90 (ddd, *J* = 7.7, 5.5, 1.3 Hz)	8.38 (td, *J* = 8.0, 1.6 Hz)	8.73 (d, *J* = 8.2 Hz)
1	CD_3OD	9.21 (d, *J* = 4.6 Hz)	7.80 (t, *J* = 8.0 Hz)	8.29 (t, *J* = 7.7 Hz)	8.63 (d, *J* = 7.5 Hz)
4Ru	$CDCl_3$	9.03 (d, *J* = 5.3 Hz)	7.87 (ddd, *J* = 7.6, 5.9, 1.0 Hz)	8.40 (t, *J* = 7.8 Hz)	8.68 (d, *J* = 8.1 Hz)
4Ru	$(CD_3)_2CO$	9.36 (d, *J* = 5.2 Hz)	8.01 (t, *J* = 6.2 Hz)	8.55 (t, *J* = 7.9 Hz)	8.87 (d, *J* = 8.1 Hz)
4Ru	CD_3OD	9.14 (dd, *J* = 5.6, 0.7 Hz)	7.90 (ddd, *J* = 7.5, 5.6, 1.3 Hz)	8.45 (td, *J* = 8.0, 1.4 Hz)	8.78 (d. *J* = 8.1 Hz)
3Me	CD_3OD	9.02 (d, *J* = 5.2 Hz)	7.72 (t, *J* = 6.6 Hz)	8.26 (td, *J* = 8.0, 1.2 Hz)	8.59 (d, *J* = 7.8 Hz)
3Et	$CDCl_3$	9.01 (dd, *J* = 5.5, 0.7 Hz)	7.56 (ddd, *J* = 7.5, 5.5, 1.2 Hz)	8.05 (td, *J* = 7.9, 1.5 Hz)	8.18 (d, *J* = 8.1 Hz)
3H	$(CD_3)_2CO$	9.05 (d, *J* = 5.1 Hz)	7.77 (ddd, *J* = 7.5, 5.5, 1.1 Hz)	8.29 (td, *J* = 7.9, 1.6 Hz)	8.64 (d, *J* = 8.2 Hz)
5	$CDCl_3$	9.00 (dd, *J* = 5.4, 0.7 Hz)	7.54 (ddd, *J* = 7.5, 5.5, 1.2 Hz)	8.01 (td, *J* = 7.9, 1.6 Hz)	8.15 (d, *J* = 8.2 Hz)
5	CD_2Cl_2	8.96 (d, *J* = 5.5 Hz)	7.56 (ddd, *J* = 7.5, 5.5, 1.3 Hz)	8.06 (td, *J* = 7.9, 1.5 Hz)	8.19 (d, *J* = 8.1 Hz)

Table 2. ^{13}C NMR resonances of the CO carbons in the Ru(II)-carbonyl compounds.

Compound	Solvent	chemical shift (ppm)]	Ref
1	$CDCl_3$	195.8	This work (see also refs 34, 40)

2	$CDCl_3$	190.4, 195.4	This work (see also ref 34)
3Me	$CDCl_3$	193.7; 198.2 (COOMe)	34
3Et	$CDCl_3$	193.3; 198.5 (COOEt)	15
4Ru[a]	$(CD_3)_2CO$	183.9 (*trans* to Cl), 187.9 (*trans* to bpy), 188.1 (anion)	This work
4Cl	CD_3OD	184.1, 188.0	40
4PF$_6$	$(CD_3)_2CO$	183.7 (*trans* to Cl), 187.7 (*trans* to bpy)	This work
5	CD_2Cl_2	201.4	This work
9	CD_2Cl_2	196.5; 196.2	This work

[a] To be noted that ref. 15 reports a single carbonyl resonance for this species at 187.2 ppm ($CDCl_3$).

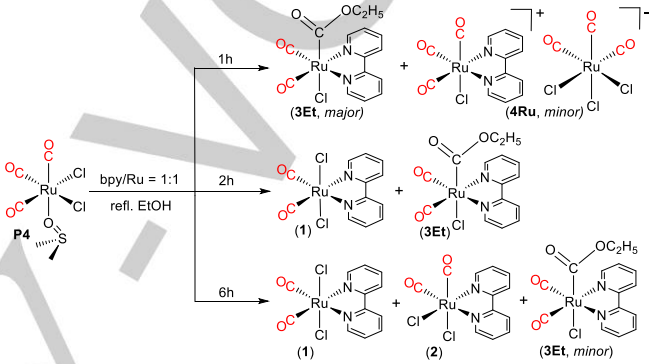
A rigorously light protected solution of **1** in $CDCl_3$ is indefinitely stable (weeks). However, exposure to diffuse indoor light is sufficient for inducing the progressive formation (days) of a brick-red precipitate on the NMR tube wall, totally insoluble in chloroform (no new resonances appear), that was not investigated. Most likely it is the known chloride-bridged dinuclear species $[Ru(bpy)Cl(CO)(\mu\text{-}Cl)]_2$ (**8**) originated by photo-induced decarbonylation of **1** (see above). Similarly, complex **1** is stable in $(CD_3)_2CO$ in the dark, whereas exposure to diffuse light induces the progressive transformation of **1** into new uncharacterized species that partially remain in solution.

3.2. Treatment of *fac*-[RuCl$_2$(CO)$_3$(dmso-O)] (P4) with bpy

The reactivity of *fac*-$[RuCl_2(CO)_3(dmso\text{-}O)]$ (**P4**) towards bpy proved to be considerably more complex and the nature of the products to depend markedly on the nature of the solvent and reaction conditions.

3.2.1. Ethanol

The treatment of **P4** with one equiv (or a slight excess) of bpy in refluxing ethanol for 1 h afforded prevalently the carboethoxy derivative *trans,cis*-$[Ru(bpy)Cl(C(O)OEt)(CO)_2]$ (**3Et**), whose X-ray structure was also determined (ESI). The coordination bond distances and angles were found to be consistent with those already published for this compound.[15]
Consistent with the geometry found in the solid state (i.e. bpy is in a symmetrical environment), only four bpy resonances are observed in the ^{1}H NMR spectrum of **3Et** in $CDCl_3$ (beside those of the –Et fragment at δ = 3.97 (CH_2, q) and 0.94 (CH_3, t)). Under these conditions, the scarcely soluble compound **4Ru** was also obtained as by-product. Upon increasing the reaction time, we found that the amount of isolated **3Et** progressively decreased (compound **4Ru** disappeared altogether) and was replaced first by *trans,cis*-$[Ru(bpy)Cl_2(CO)_2]$ (**1**) and, for prolonged reflux, also by its stereoisomer *cis,cis*-$[Ru(bpy)Cl_2(CO)_2]$ (**2**). For the longest reaction time, residual **3Et** was isolated only from the concentrated mother liquor. Our results, summarized in Scheme 19, suggest that **3Et** is an intermediate in the formation of **1** and **2** and are basically consistent with literature data concerning the reactivity of the dinuclear precursor $[RuCl_2(CO)_3]_2$ (**P1**) with bpy in refluxing alcoholic solvents (see above).[15,34].

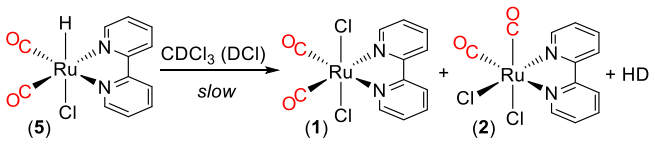


Scheme 19. Reactions of the tricarbonyl precursor **P4** with bpy in refluxing EtOH: the nature of the products depends on the reaction time.

3.2.2. Acetone

When an acetone solution of **P4** was treated with a four-fold excess of bpy at room temperature it turned rapidly deep-orange, with formation of a small amount of red-orange crystals. X-ray analysis showed them to be composed by the Ru(I) dimer [*cis*-$Ru(bpy)Cl(CO)_2]_2$ (**6**) in the gauche conformation. The same species had been previously isolated by Pakkanen and coworkers upon treatment of $[RuCl_2(CO)_3]_2$ (**P1**) with an excess of bpy in diethylene glycol at 100°C.[34] Despite the low quality of the X-ray data (ESI), the main geometrical features of our compound are consistent with those reported in the literature.
Moreover, after removal of the precipitate, light orange-reddish crystals formed from the mother liquor upon addition of diethyl ether to the point of cloudiness. The ^{1}H NMR spectrum of this species in $CDCl_3$ (four bpy resonances in the downfield region, implying that bpy is in a symmetrical environment, and a sharp singlet at δ = –11.31) is consistent with that reported in the literature for the hydrido complex *trans,cis*-$[Ru(bpy)ClH(CO)_2]$ (**5**).[34] We found that a light-protected $CDCl_3$ solution of compound **5** is unstable at room temperature: Within 2 days, the NMR resonances of **5** were almost completely replaced by those of a mixture of the dichlorido isomers *trans,cis*-$[Ru(bpy)Cl_2(CO)_2]$ (**1**) and *cis,cis*-$[Ru(bpy)Cl_2(CO)_2]$ (**2**) (ca. 3:2 ratio, ESI), indicating that the H^- ligand of **5** was slowly replaced by Cl^- ions coming from the solvent. Pakkanen and coworkers had reported the conversion of **5** into **1** upon treatment with concentrated

HCl.[15,34] Most likely in our case **5** reacts with DCl, always present is small amounts in $CDCl_3$, with formation of HD (not detected) and of the two isomeric complexes (Scheme 20).



Scheme 20. The slow spontaneous conversion of the hydrido complex **5** into a mixture of **1** and **2** in $CDCl_3$.

Since we established that pure **1** is stable in $CDCl_3$ solution in the dark, the formation of **2** from **5** involves the presence of a common – most likely five coordinate – intermediate. In the less acidic CD_2Cl_2, formation of **1** and **2** from **5** is much slower (days) and is accompanied by precipitation of dimer **6** for prolonged observation periods. More interestingly, the NMR spectra showed that in this solvent – prior to the occurrence of the above mentioned processes – partial isomerization of **5** to another hydrido complex (**9**, characterized by a singlet at δ = –10.44, vs. δ = –11.03 for **5**) occurs within a few hours in the dark (Figure 2).

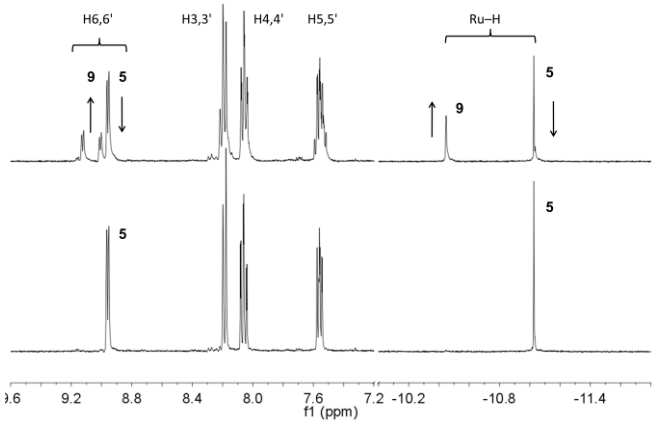
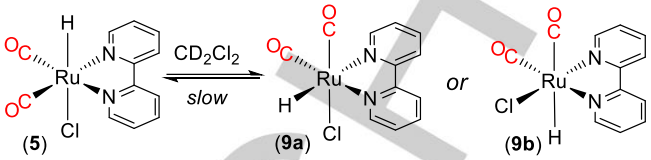


Figure 2. ^{1}H NMR spectrum of *trans,cis*-[Ru(bpy)ClH(CO)$_2$] (**5**) in CD_2Cl_2 immediately after dissolution (bottom) and after 48 h (top), with the resonances of the new hydrido complex **9**.

Consistent with the presence of two resolved doublets for H6 and H6' (δ = 9.12 and 9.01, J = 5 Hz), typical of bpy in an asymmetrical environment (all other bpy resonances are overlapped with those of residual **5**), an all-*cis* geometry was assigned to the new compound: *cis,cis*-[Ru(bpy)ClH(CO)$_2$] (**9**, Scheme 21). In the spectrum of **9** the two doublets of H6 and H6' are not widely spaced (Figure 2), as they are in the case of **2**, suggesting that neither proton points towards the coordinated chloride (see above). For this reason we favor the isomer **9a**, in which H is *trans* to N of bpy, with respect to **9b**, even though an unambiguous structural determination could not be performed.



Scheme 21. Partial isomerization of *trans,cis*-[Ru(bpy)ClH(CO)$_2$] (**5**) into *cis,cis*-[Ru(bpy)ClH(CO)$_2$] (**9**). The two possible stereoisomers of **9** (of which we favor **9a**) are shown.

When the precursor **P4** was treated with one eq. of bpy in acetone at room temperature (either in the dark or in the presence of indoor diffuse light), the colorless solution turned rapidly pale pink and remained unchanged afterwards. Colorless crystals formed within a few days upon addition of diethyl ether to the point of cloudiness. This product was unambiguously identified as the ion-pair complex *fac*-[Ru(bpy)Cl(CO)$_3$]$^+$*fac*-[RuCl$_3$(CO)$_3$]$^-$ (**4Ru**) from the ^{1}H and ^{13}C NMR spectra in CD_3OD and $(CD_3)_2CO$ (where it is well soluble) and its nature was also confirmed by an X-ray structure determination (Figure 3). When the same reaction was performed in $CHCl_3$ the crystals of **4Ru** formed spontaneously, since the complex is sparingly soluble in this solvent.[59] The formation of the ion-pair complex **4Ru**, that leaves half eq of bpy unreacted, suggests that chloride is a very strong competitor for the coordination to **P4** (or, in general, to a *fac*-{RuCl$_2$(CO)$_3$} intermediate).

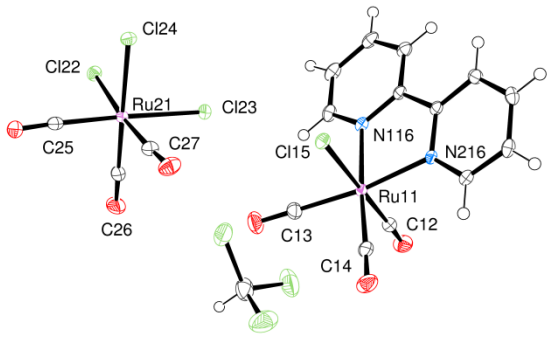


Figure 3. X-ray molecular structure (50% probability ellipsoids) of *fac*-[Ru(bpy)Cl(CO)$_3$]$^+$*fac*-[RuCl$_3$(CO)$_3$]$^-$·$CHCl_3$ (**4Ru**).

The ^{1}H NMR spectrum of **4Ru** consists only of four bpy resonances (Table 1) and in $(CD_3)_2CO$ it remains unchanged for days – also when exposed to diffuse indoor light. The ^{13}C NMR spectrum shows (besides the five resonances for coordinated bpy) three carbonyl peaks in ca. 1:2:3 ratio: the most intense peak at 188.1 is attributed to the three equivalent carbonyls of the anion (see also below). Of the two remaining peaks, pertaining to the cationic fragment, the least intense at 183.9 is attributed to the CO *trans* to Cl, and the remaining one at 187.9

to the two carbonyls *trans* to bpy. In CD_3OD solution compound **4Ru** rapidly equilibrates with a new minor species (ca 10%), characterized by four new bpy resonances – each ca. 0.1 – 0.2 ppm upfield from the corresponding one in **4Ru** – attributed to *trans,cis*-[Ru(bpy)Cl(C(O)OCD_3)$(CO)_2$] (**3Me**). The resonances of **3Me** were found to grow very slowly with time (days), but they increased within minutes at the expenses of those of **4Ru** upon addition of a few μL of a 0.1 M NaOD solution in D_2O, thus confirming the attribution. For longer reaction times (hours) also the resonances of the dichlorido isomers **1** and **2** appeared, even though **3Me** remained the main species in solution. A similar behavior was observed in $(CD_3)_2CO$ upon addition of a small amount of the NaOD solution: a new set of four bpy signals attributed to the hydroxycarbonyl species *trans,cis*-[Ru(bpy)Cl(C(O)OD)$(CO)_2$] (**3H**) – each ca. 0.2 – 0.3 ppm upfield from the corresponding one in **4Ru** – grew rapidly. Within two hours the resonances of both **4Ru** and **3H** were completely replaced by those of a ca 1:2 mixture of the neutral isomers **1** and **2**. The formation of **1** and **2** from **3Me** and **3H** involves the presence of free Cl^-, which is set free from the *fac*-$[RuCl_3(CO)_3]^-$ anion upon attack of OD^-. Our findings are consistent with **3H** being much less stable than **3R** towards chloride attack.

It is absolutely remarkable that nucleophilic attack of both CH_3O^- and OH^- on *fac*-$[Ru(bpy)Cl(CO)_3]^+$ occurs selectively on the carbonyl *trans* to Cl: only in this case bpy remains in a symmetrical environment.

We also found that addition of an excess of N(*n*-hexyl)$_4$Cl to a $(CD_3)_2CO$ solution of **4Ru** does NOT lead to the formation of the yellow isomers **1** and **2** at room temperature, but rather to the slow precipitation of colorless microcrystals of *fac*-[Ru(bpy)Cl$(CO)_3$]Cl (**4Cl**), as confirmed by the X-ray structure determination (Figure 4). In other words this finding confirms that Cl^- is unable to replace directly a CO on *fac*-$[Ru(bpy)Cl(CO)_3]^+$ under mild conditions. On the contrary, we have shown that it replaces the hydrido in **5**, the methoxycabonyl group in **3Me** and – much more easily – the hydroxycarbonyl group in **3H**. Consistent with this finding, upon increasing the bpy:**P4** ratio from 1 to 2 in the preparation (i.e. a more basic environment), a mixture of **4Ru** (well soluble in acetone) and **4Cl** (almost insoluble in acetone) was obtained.

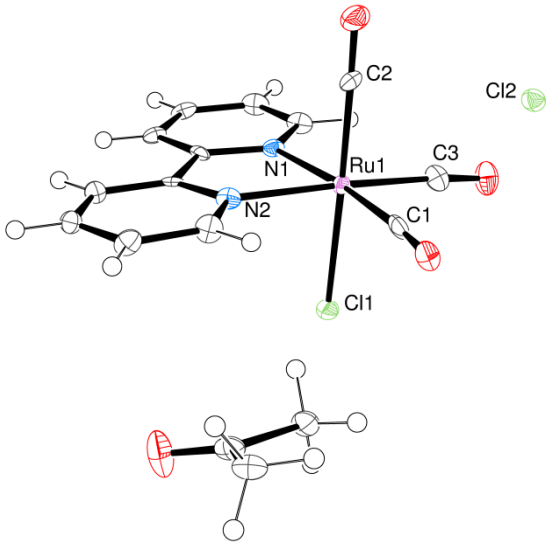


Figure 4. X-ray molecular structure (50% probability ellipsoids) of *fac*-[Ru(bpy)Cl$(CO)_3$]Cl·$(CH_3)_2CO$ (**4Cl**).

When the reaction between **P4** and bpy (1 eq) was performed in the presence of 1 eq of $AgPF_6$ the PF_6 salt of **4**, that is *fac*-[Ru(bpy)Cl$(CO)_3$][PF_6] (**4PF$_6$**), was isolated. The ^{13}C NMR spectrum of **4PF$_6$** in $(CD_3)_2CO$ is equal to that of **4Ru** except for the absence of the most downfield and intense carbonyl peak at δ = 188.1, that is thus unambiguously attributed to the *fac*-$[RuCl_3(CO)_3]^-$ fragment (see above). Similar results were obtained using $AgSbF_6$; the X-ray structure of **4SbF$_6$** is reported in Figure 5.

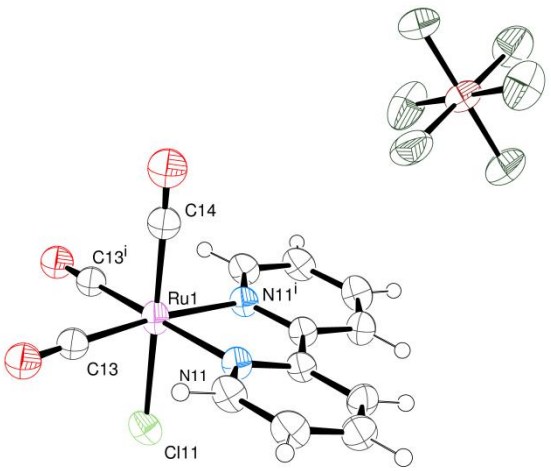
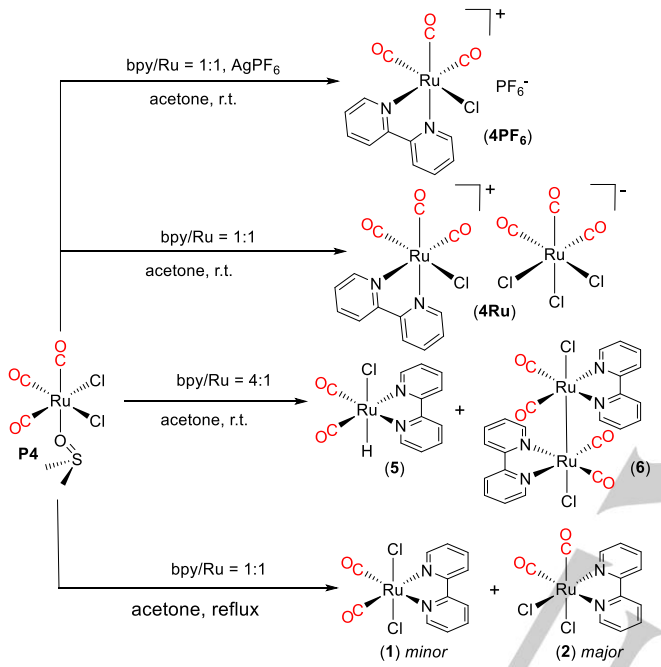


Figure 5. X-ray molecular structure (50% probability ellipsoids) of *fac*-[Ru(bpy)Cl$(CO)_3$][SbF_6] (**4SbF$_6$**). Only one of the three independent molecules of the elementary cell is shown. The molecules of crystallization (1/3 $(CH_3)_2CO$ and 2/3 H_2O) are also omitted.

Finally, treatment of **P4** with one equivalent of bpy in refluxing acetone afforded, beside some precipitate of dimer **6**, a mixture of the two neutral isomers **1** and **2**, with **2** prevailing. Prolonging the reaction time from 30 to 60 min led to an increase of the ratio between **2** and **1**, from 3:1 to 7:1. This result, together with that in refluxing ethanol (see above), suggests that **2** is the thermodynamically more stable isomer.
Overall, the reactivity between precursor **P4** and bpy in acetone is summarized in Scheme 22.

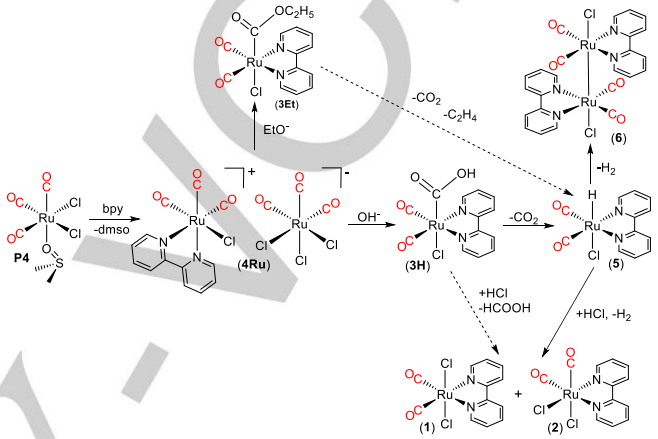


Scheme 22. Reactions of the tricarbonyl precursor **P4** with bpy in acetone: the nature of the products depends on the bpy/Ru ratio and on the reaction temperature.

4. Conclusions

The conclusions reported below concern the investigated bpy derivatives, but we are confident that they are quite general and can be extended to most chelating diimine ligands.
From a synthetic point of view, the Ru(II)-dmso carbonyls **P3** and **P4** are probably not competitive with the literature precursors **P1** and **P2** because their preparations require additional synthetic steps from hydrated $RuCl_3$: Whereas both **P1** and **P2** are obtained in a single step from the universal ruthenium precursor, **P3** and **P4** are obtained in three and two steps, respectively.[24] In addition, in terms of general reactivity, **P3** is largely comparable to **P2**, and **P4** to **P1**. Nevertheless, from a mechanistic point of view, **P3** and **P4** proved to be very valuable precursors. In fact, being they well defined species and – above all – 'activated forms' of **P2** and **P1**, respectively, they allowed us to perform reactions under relatively mild conditions and to gain a mechanistic insight that previously had escaped full understanding despite the extensive investigation performed.

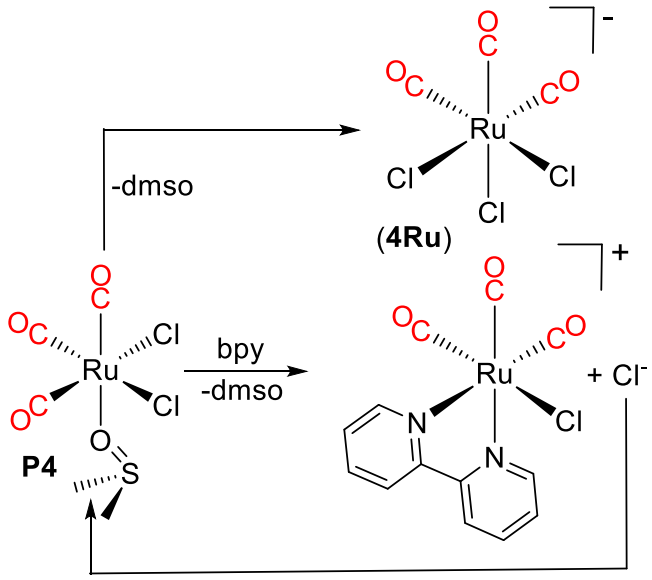
The dicarbonyl complex *trans,cis,cis*-[$RuCl_2(CO)_2$(dmso-O)$_2$] (**P3**) proved to be an excellent precursor for the selective preparation, under mild conditions, of *trans,cis*-[Ru(bpy)$Cl_2(CO)_2$] (**1**) (see also below).
The results obtained from the tricarbonyl precursor *fac*-[$RuCl_2(CO)_3$(dmso-O)] (**P4**) in various conditions are more complex and deserve a detailed discussion. Our findings are rationalized by the network of reactions reported in Scheme 23.



Scheme 23. Comprehensive network of reactions accounting for the Ru(II) products isolated upon treatment of the tricarbonyl precursor **P4** with bpy.

All our findings consistently indicated that the two neutral dichlorido isomers *trans,cis*-[Ru(bpy)$Cl_2(CO)_2$] (**1**) and *cis,cis*-[Ru(bpy)$Cl_2(CO)_2$] (**2**) are the thermodynamic sink of the reactions of **P4** with bpy. They are always the prevailing products when the reaction temperature and/or time are increased, regardless of the solvent. In addition, we notice that all the kinetic products, i.e. those obtained for short reaction times and/or low temperatures – *trans,cis*-[Ru(bpy)Cl(C(O)OEt)$(CO)_2$] (**3Et**), *trans,cis*-[Ru(bpy)ClH$(CO)_2$] (**5**), and the Ru(I) dimer [*cis*-Ru(bpy)Cl$(CO)_2]_2$ (**6**) – have only one chloride in the coordination sphere of ruthenium, suggesting that they derive from a common intermediate, the cationic tricarbonyl species *fac*-[Ru(bpy)Cl$(CO)_3]^+$. This complex had been previously obtained by Pakkanen and co-workers both as the ion-pair complex *fac*-[Ru(bpy)Cl$(CO)_3]^+$*fac*-[$RuCl_3(CO)_3]^-$ (**4Ru**) and as the chloride salt (**4Cl**, also characterized through the X-ray structure),[15,40] but not explicitly recognized as *the key intermediate*. We found that complex **4Ru** is the main product when the reaction between **P4** and 1 eq of bpy is performed at room temperature in acetone or DCM. Therefore, in the very first reaction with **P4**, bpy replaces the labile dmso-O and one chloride generating the cation *fac*-[Ru(bpy)Cl$(CO)_3]^+$. However, the chloride ion released in this step competes effectively with bpy for binding to the tricarbonyl precursor and – unless it is removed by addition of a silver salt – generates the anion *fac*-[$RuCl_3(CO)_3]^-$ in a parallel reaction. In conclusion, ½ eq of bpy remains unreacted and the ion pair complex *fac*-[Ru(bpy)Cl$(CO)_3]^+$*fac*-[$RuCl_3(CO)_3]^-$ (**4Ru**) is isolated. This *chloride rebound mechanism* (Scheme 24) basically leads to a

waste of ruthenium, since the symmetrical anion (that can be seen also as a temporary storage site for chloride, see below) does not react with bpy.



Scheme 24. The *chloride rebound mechanism* leading to the formation of **4Ru**.

We found that, at room temperature, Cl^- – even when in large excess – is unable to replace a carbonyl on *fac*-$[Ru(bpy)Cl(CO)_3]^+$. On the other hand, one carbonyl of this activated cation – that is otherwise stable – can easily undergo a nucleophilic attack from RO^- or OH^- generating compounds **3R** and **3H**, respectively. As noted above, the nucleophilic attack on *fac*-$[Ru(bpy)Cl(CO)_3]^+$ occurs selectively on the carbonyl *trans* to Cl. The reason for this selectivity is still unclear at the moment. X-ray structural data are now available for six *fac*-$[Ru(bpy)Cl(CO)_3]^+$ cations: Five from this work (**4Ru**, **4Cl** and the three independent units in **4SbF$_6$**, ESI) and one for **4Cl** (obtained with a different synthetic procedure) from ref. 40. An exam of the Ru–CO bond distances (ESI) shows that in three cations (**4Ru** and **4Cl** × 2) the ruthenium–carbonyl bond *trans* to Cl is shorter than the two others, whereas in the other three it is undistinguishable or even longer, suggesting that these distances are strongly influenced by the nature of the anion, i.e. by the crystal packing. In other words, the solid state data do not allow us to establish if there is any significant difference in terms of π-back bonding (and therefore in reactivity) among the three carbonyls. We are currently performing theoretical calculations and simulations on this system, whose results will be reported in a subsequent paper.

Not surprisingly, the electron-poor tricarbonyl cation *fac*-$[Ru(bpy)Cl(CO)_3]^+$ is more prone to nucleophilic attack than the neutral di- and tricarbonyl species **P1** – **P4**, **1**, and **2** (see above). To be noted that an increase in the bpy/**P4** ratio has two opposite effects: From one hand it improves the competition with Cl^-, but from the other – acting as a base – it increases the equilibrium concentration of the nucleophile (RO^- in alcoholic solvents or OH^- from adventitious water in other solvents) that attacks *fac*-$[Ru(bpy)Cl(CO)_3]^+$. In addition, the nucleophile attacks also the *fac*-$[RuCl_3(CO)_3]^-$ anion releasing the chloride,[43] and thus leading eventually to the formation of the dead-end products **1** and **2**. Decarbonylation of **3H** (or of **3R**, followed by β-H elimination) leads to the formation of the hydride complex **5**. We have shown that Cl^- replaces easily H^- in **5**, leading to a mixture of **1** and **2**. Presumably Cl^- is also capable of replacing directly the anionic carboxylate ligand in **3R** and **3H**, without the need of going through compound **5**. In conclusion, once the cation *fac*-$[Ru(bpy)Cl(CO)_3]^+$ has undergone nucleophilic attack with generation of **3R** or **3H** (or eventually **5**), the formation of **1** and **2** is unavoidable, unless there is no free chloride in the medium.

All our experimental evidence suggests that, also at higher temperatures, replacement of a carbonyl of *fac*-$[Ru(bpy)Cl(CO)_3]^+$ by Cl^- does not occur directly, but exclusively through the nucleophilic attack route.

Finally, the formation of the dinuclear Ru(I)–Ru(I) byproduct **6** has been explained as a result of reductive elimination of H_2 from two units of **5**. A similar hypothesis had been advanced by Bera and co-workers for the formation of the dinuclear Ru(I)–Ru(I) cation *fac*-$[Ru(CH_3CN)_3(CO)_2]_2^{2+}$ upon treatment of **P1** with KOH and TlO_3SCF_3 (for the complete removal of the chlorides) in refluxing acetonitrile.[60] As an alternative, and remembering that formation of **6** occurs in a basic environment due to the excess of bpy, we might hypothesize that the hydride **5** has an amphoteric nature: in acidic medium (e.g. in $CDCl_3$ containing DCl) it behaves as a base and releases H^- (that reacts with H^+ generating H_2), whereas in basic medium it behaves as an acid and releases H^+ (that reacts with OH^-) and a Ru(I) fragment that generates **6**.

We notice that when the coordination of bpy occurs on the dicarbonyl precursor **P3**, the *trans* geometry of the two chlorides is basically maintained and compound **1** is the largely prevailing product under all the conditions investigated (regardless of the reaction temperature and bpy:Ru ratio). Conversely, when the neutral dichloro species are obtained from **P4**, as a consequence of the chloride rebound mechanism through the nucleophilic attack route, all our findings suggest that **1** is the kinetic product of the reaction, whereas its isomer **2** is the thermodynamically more stable product. This difference is not surprising, since the reaction pathways involve different intermediates and confirms that **1**, once formed, does not interconvert easily to its more stable isomer **2**.

In conclusion, coordination of bpy to **P1** (or **P4**) activates the $\{RuCl_2(CO)_3\}$ fragment by generating the tricarbonyl cation *fac*-$[Ru(bpy)Cl(CO)_3]^+$. This activated key intermediate leads – through the facile and selective nucleophilic attack on the CO *trans* to Cl – to all other species. It should be noted that the nucleophilic attack of OH^- onto a Ru(II)-carbonyl intermediate is one of the key steps in the catalytic mechanisms proposed for both WGSR and CO_2 reduction, and hydroxycarbonyl species are believed to be important intermediates in both catalytic cycles.[43] For this reason, and given the chloride-avidity of **3H** (as well as of **3R** and **5**), we suggest that the catalytic activity of

complexes such as *fac*-[Ru(bpy)Cl(CO)$_3$][PF$_6$] (**4PF$_6$**) should be investigated in a chloride-free environment.

Experimental Section

Materials

All chemicals were purchased from Sigma-Aldrich and used as received. Solvents were of reagent grade and were previously dried over activated molecular sieves (3 Å). The precursors *trans,cis,cis*-[RuCl$_2$(CO)$_2$(dmso-O)$_2$] (**P3**) and *fac*-[RuCl$_2$(CO)$_3$(dmso-O)] (**P4**) were synthesized as previously described by us.[24]

Instrumental methods

Mono- (^{1}H (400 or 500 MHz), ^{13}C (125.7 MHz)) and bi-dimensional (^{1}H-^{1}H COSY, ^{1}H-^{13}C HSQC) NMR spectra were recorded on a JEOL Eclipse 400FT or on a Varian 500 spectrometer. All spectra were run at room temperature (r.t.); ^{1}H chemical shifts were referenced to the peak of residual non-deuterated solvent (δ = 7.26 for $CDCl_3$, 5.32 for CD_2Cl_2 , 2.05 for $(CD_3)_2CO$, and 4.87 CD_3OD); ^{13}C chemical shifts in CD_3Cl they were referenced to the peak of residual non-deuterated solvent (δ = 77.16 for $CDCl_3$, 54.00 for CD_2Cl_2, 39.52 for $(CD_3)_2CO$, and 49.00 for CD_3OD). UV-vis spectra were obtained at 25°C on a Jasco V-500 UV-vis spectrophotometer equipped with a Peltier temperature controller, using 1.0 cm path-length quartz cuvettes (3.0 mL). Elemental analysis was performed at the Department of Chemistry of the University of Bologna (Italy). For X-ray diffraction see ESI.

Synthesis of the complexes.

This work was aimed at understanding the reactivity of the precursors **P3** and **P4**. In addition, basically all the products are already known and synthetic procedures are reported for them in the literature using the known **P1** and **P2** as precursors. Finally, the products were often obtained as mixtures, whose components were identified but no attempt was done to separate them quantitatively. For these reasons, in many cases we did not optimize the synthetic procedures and herein only the most relevant examples are reported. When different synthetic procedures afforded the same product, only one representative example is reported.

***trans,cis*-[Ru(bpy)Cl$_2$(CO)$_2$] (1).**

A 50.0 mg amount of *trans,cis,cis*-[RuCl$_2$(CO)$_2$(dmso-O)$_2$] (**P3**, 0.13 mmol) was partially dissolved in 10 mL of absolute ethanol. A slight excess of bpy (22.0 mg, 0.14 mmol) was added and the mixture was refluxed for 4 h in the dark. A clear solution was rapidly obtained upon warming, from which a small amount of a pale yellow fluffy precipitate began to form after ca. 30 min of reflux. Upon cooling the amount of precipitate rapidly increased. It was removed by filtration after overnight standing at room temperature, washed with cold ethanol and diethyl ether and dried *in vacuo* (38.0 mg, yield 76%). The product was pure **1** according to the ^{1}H NMR spectrum. Found: C, 37,44; H, 2.15; N, 7.20%. $C_{12}H_8N_2Cl_2O_2Ru$ (384.18) requires C; 37.51; H; 2.09; N, 7.29%. A second batch of **1** (ca. 10 mg) was obtained from the mother liquor upon concentration and addition of diethyl ether; according to the ^{1}H NMR spectrum this batch contained ca. 10% of the isomer **2**.

Similar results were obtained when the reaction was performed in methanol, either at room temperature (24 h) or at reflux (2 and 4 h). In these cases, only the yield of pure **1** in the first batch was lower, ranging from 44 to 58%.

^{13}C{^{1}H} NMR spectrum (acetone-d_6): 124.3 (C3,3'), 127.5 (C5,5'), 140.7 (C4,4'), 153.3 (C6,6'); ($CDCl_3$): 123.2 (C3,3'), 127.5 (C5,5'), 139.6 (C4,4'), 153.1 (C6,6'), 155.1 (C2,2'), 195.8 (CO). UV-vis spectrum in $CHCl_3$ (λ_{max} (nm), ε): 363 (1680).

***cis,cis*-[Ru(bpy)Cl$_2$(CO)$_2$] (2).**

Mixtures of **2** and of its isomer **1** were obtained upon prolonged reflux of **P4** and bpy in ethanol or acetone. An example is detailed below. No attempts were done to prepare (or isolate) this complex in pure form.

A 100.0 mg amount of *fac*-[RuCl$_2$(CO)$_3$(dmso-O)] (**P4**, 0.30 mmol) was partially dissolved in 10 mL of absolute ethanol. A slight excess of bpy (70.1 mg, 0.45 mmol, bpy/Ru = 1.5) was added and the mixture (light protected) was refluxed for 6 h, yielding a deep yellow solution. After cooling, a crystalline yellow-orange solid formed within a few hours. After 48 h it was removed by filtration, washed with cold ethanol and diethyl ether and dried *in vacuo* (34.0 mg). According to the ^{1}H NMR spectrum, the product was a ca. 1:1 mixture of **1** and **2**. A second fraction of solid (23 mg) was obtained from the mother liquor upon concentration and addition of diethyl ether; according to the ^{1}H NMR spectrum this fraction contained a ca. 1:1 mixture of **1** and **3Et**.

^{1}H NMR spectrum (acetone-d_6): 9.56 (H6, d, J = 6.4), 9.02 (H6', d, J = 6.4 Hz), 8.70/8.66 (H3/H3' partially overlapped with H3,3' of **1**, d), 8.39 (H4 partially overlapped with H4,4' of **1**, t, J = 7.7 Hz), 8.27 (H4', t, J = 7.7 Hz), 7.91 (H5, t, J = 6.6 Hz), 7.71 (H5', t, J = 6.7 Hz); (CD_3OD): 9.56 (H6, d, J = 4.0), 8.95 (H6', d, J = 4.2 Hz), 8.60 (H3+H3' partially overlapped with H3,3' of **1**, d), 8.33 (H4 partially overlapped with H4,4' of **1**, t, J = 7.6 Hz), 8.22 (H4', t, J = 7.6 Hz), 7.86 (H5, t, J = 5.6 Hz), 7.65 (H5', t, J = 5.6 Hz). ($CDCl_3$): 9.72 (H6, d, J = 5.1 Hz), 8.83 (H6', d, J = 5.4 Hz), 8.25 (H3+H3' overlapped with H3,3' of **1**, d, J = 8.1 Hz), 8.13 (H4, t, J = 7.9), 8.06 (H4', t, J = 7.9), 7.70 (H5, m), 7.52 (H5', m). ^{13}C{^{1}H} NMR spectrum (acetone-d_6): 124.1, 124.4 (C3,3'), 127.0 (C5), 128.0 (C5'), 140.0 (C4'), 140.8 (C4), 149.8 (C6), 156.4 (C6'); ($CDCl_3$): 123.1, 123.8 (C3,3'), 127.1 (C5), 127.6 (C5'), 139.2 (C4'), 140.0 (C4), 150.8 (C6), 154.9 (C6'), 155.7, 156.2 (C2,2'), 189.9, 194.7 (CO).

***trans,cis*-[Ru(bpy)Cl(C(O)OEt)(CO)$_2$] (3Et).**

Mixtures of **3Et** and of **1** were obtained upon refluxing **P4** and bpy in ethanol. An example is detailed below. No attempts were done to isolate this complex quantitatively in pure form.

A 100.0 mg amount of *fac*-[RuCl$_2$(CO)$_3$(dmso-O)] (**P4**, 0.30 mmol) was partially dissolved in 10 mL of absolute ethanol. A slight excess of bpy (70.3 mg, 0.45 mmol, bpy/Ru = 1.5) was added and the (light protected) mixture was refluxed for 2 h. After cooling, the deep yellow solution was rotary-evaporated to ca. ½ volume. Yellow-orange crystals formed overnight; a few of them were fished out of the solution and, according to the ^{1}H NMR spectrum and X-ray diffraction, were pure **3Et**. The bulk of

the precipitate was then removed by filtration, washed with a minimum amount of cold ethanol and diethyl ether and dried *in vacuo* (63.5 mg). According to the ^{1}H NMR spectrum, the product was a ca. 1:3 mixture of **1** and **3Et**.

***fac*-[Ru(bpy)Cl(CO)$_3$]$^+$*fac*-[RuCl$_3$(CO)$_3$]$^-$ (4Ru).**

A 50.0 mg amount of *fac*-[RuCl$_2$(CO)$_3$(dmso-O)] (**P4**, 0.15 mmol) was dissolved in 3 mL of acetone. Upon addition of 1 eq of bpy (25.0 mg, 0.16 mmol), the colorless solution turned immediately pale-pink. After 24 h, diethyl ether was progressively added dropwise until reaching the point of cloudiness. A moderate amount of very pale pink crystals formed within 48 h and were then removed by filtration, washed with diethyl ether and dried *in vacuo* (25.0 mg, 49.8% with respect to bpy). Found: C, 28.88; H, 1.25; N, 4.30%. $C_{16}H_8N_2Cl_4O_6Ru_2$ (668.20) requires C; 28.76; H; 1.21; N, 4.19%.

When the reaction was performed in chloroform instead of acetone (100.0 mg of **P4**, 50.0 mg of bpy, 5 mL of $CHCl_3$) a small amount of almost colorless crystals of **4** grew spontaneously from the pale-pink solution within 48 h. They were fished out of the solution and submitted to X-ray analysis. No yield was calculated in this case.

^{13}C{^{1}H} NMR spectrum (acetone-d_6): 188.1 (3 CO anion), 187.9 (2 CO *trans* to bpy), 183.9 (CO *trans* to Cl), 156.4 (C2/2'), 155.8 (C6/6'), 143.3 (C4/4'), 129.7 (C5/5'), 126.7 (C3/3').

***fac*-[Ru(bpy)Cl(CO)$_3$][Cl] (4Cl).**

This compound was obtained in the NMR tube upon addition of an excess N(*n*-hexyl)$_4$Cl to a $(CD_3)_2CO$ solution of **4Ru**. Pale-pink (almost colorless) crystals of **4Cl** formed on the tube wall and were fished out for X-ray analysis. Crystal formation was coincident with the progressive disappearance of the original resonances from the NMR spectrum, suggesting that precipitation of the anion was basically complete. Found: C, 41.05; H, 2.90; N, 5.87%. $C_{13}H_8N_2Cl_2O_3Ru\cdot(CH_3)_2CO$ (470.27) requires C; 40.86; H; 3.00; N, 5.95%.

***fac*-[Ru(bpy)Cl(CO)$_3$][PF$_6$] (4PF$_6$).** A 50.0 mg amount of *fac*-[RuCl$_2$(CO)$_3$(dmso-O)] (**P4**, 0.15 mmol), dissolved in 2 mL of DCM, was added dropwise under stirring to an acetone solution (2 mL) in which 25.0 amount of bpy (0.15 mmol) and 38.0 mg of $AgPF_6$ (0.15 mmol) were dissolved. A brown precipitate formed immediately. After 30 min, filtration over a celite pad (thoroughly washed with acetone) afforded a clear pink-orange solution. The solvent was removed under vacuum (at room temperature) and replaced with 2 mL of DCM, affording a pink-orange precipitate and a pale orange solution. The precipitate was removed by filtration, washed with DCM and diethyl ether and dried *in vacuo* (52.0 mg, 66.5%). According to ^{1}H NMR spectroscopy, the raw material contained a minor amount (ca. 5%) of **3H**. Recrystallization from acetone/diethyl ether afforded pure **4PF$_6$** (yield 60%). Found: C,29.78; H, 1.60; N, 5.42%. $C_{13}H_8N_2ClO_3PF_6Ru$ (521.70) requires C; 29.93; H; 1.55; N, 5.37%. ^{31}P NMR spectrum (acetone-d_6): -143.6 (ept, $J_{P\text{-}F}$ = 707.5 Hz).

The corresponding SbF_6 derivative (**4SbF$_6$**) was obtained with the same procedure. Crystals of **4SbF$_6$** suitable for X-ray diffraction were obtained upon layering diethyl ether on an acetone solution of the complex.

***trans,cis*-[Ru(bpy)ClH(CO)$_2$] (5) and [*cis*-Ru(bpy)Cl(CO)$_2$]$_2$ (6).**

A 100.0 mg amount of *fac*-[RuCl$_2$(CO)$_3$(dmso-O)] (**P4**, 0.30 mmol) was dissolved in 5 mL of acetone and a ca. four-fold excess of bpy (192.3 mg, 1.23 mmol, bpy/Ru = 4.1) was added. A small amount of red-orange crystals (ca. 10 mg) formed within 2 h at r.t. and were removed by filtration. X-ray analysis showed them to be made of the Ru(I) dimer [*cis*-Ru(bpy)Cl(CO)$_2$]$_2$ (**6**). Found: C, 41.21; H, 2.39; N, 8.10%. $C_{24}H_{16}N_4Cl_2O_4Ru_2$ (697.46) requires C; 41.33; H; 2.31; N, 8.03%. From the concentrated mother liquor a small amount of reddish crystals grew with time and after six days were removed by filtration, washed with diethyl ether and dried *in vacuo* (27.0 mg, 25.6%). According to the ^{1}H NMR spectrum, the product was pure **5**. Found: C, 40.98; H, 2.55; N, 8.13%. $C_{12}H_9N_2ClO_2Ru$ (349.74) requires C; 41.21; H; 2.59; N, 8.01%. ^{13}C{^{1}H} NMR spectrum of **5** (CD_2Cl_2): 123.3 (C3,3'), 127.2 (C5,5'), 139.3 (C4,4'), 153.3 (C6,6'), 155.3 (C2,2'), 201.4 (CO). As detailed in the text, in DCM solution complex **5** slowly isomerizes to **9**. The NMR spectra of this latter were deduced from mixtures of **5** and **9**. ^{13}C{^{1}H} NMR spectrum of **9** (CD_2Cl_2): 123.2, 124.2 (C3,3'), 127.0, 127.5 (C5,5'), 139.1, 139.5 (C4,4'), 150.9, 153.6 (C6,6'), 156.1, 156.4 (C2,2'), 196.2, 196.5 (CO). UV-vis spectrum of **5** in CH_2Cl_2 (λ_{max} (nm), ε): 496 br (186); 355 (2175).

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Keywords: Ruthenium • Carbonyl ligands • 2,2'-bipyridine • Substitution • Mechanism

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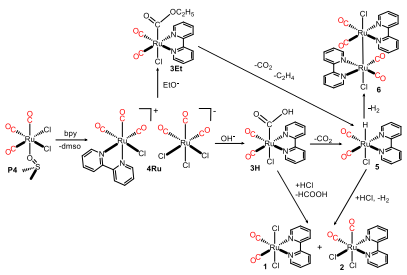
This manuscript reinvestigates the title reaction: A thorough review of the literature data is followed by our original results and finally by a detailed discussion that wraps-up old and new results in a comprehensive frame and shows that the coordination of diimines to Ru(II)-carbonyl precursors has a fairly more complex mechanism than anticipated.



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New insight into a deceptively simple reaction: the coordination of bpy to Ru(II)-carbonyl precursors. The central role of the *fac*-$[Ru(bpy)Cl(CO)_3]^+$ intermediate and the *chloride-rebound* mechanism.

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