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Tricarbonyl Re^{I} Complexes from Functionalised Pyridine–Triazole Derivatives: From Mononuclear to Unexpected Dimeric Complexes

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As a variation of the commonly used bipy ligand in $Re(CO)_3$ chemistry, a series of structurally related complexes in which bipy is replaced by pyridine–triazole ligands (or pyta) bearing a pendant acetyl group on the triazole ring were prepared efficiently by the click chemistry approach. Depending on the nature of the pendant arm, different Re^{I} complexes were obtained. Surprisingly, starting from the ligand with unprotected acetyl group yielded two structural isomers of $Re(CO)_3$ dimeric species. One isomer (compound **5a**) was isolated and characterised by X-ray crystallography. The rhenium atoms are octahedrally coordinated to three carbonyl groups in *fac* arrangement and to two nitrogen atoms of one pyta and an oxygen atom of the other. DFT calculations confirmed that the isolated isomer represents the thermodynamically favoured form. As expected, these complexes exhibited luminescence. To conclude, the unexpected formation of **5** represents an original strategy toward the synthesis of new luminescent rhenium(I) dimeric (multimeric) species.

Introduction

The ability of 2,2′-bipyridine derivatives to act as strong chelating ligands with a wide range of different transition metals is well known.[1] These metallic complexes are still attractive because of their pivotal role in materials science and in areas relating to chemistry and biology. Among these metallic complexes, rhenium(I) tricarbonyl complexes of the general formula *fac*-[Re(2,2′-bipyridine-type ligand)-$(CO)_3L]^+$, where L is an auxiliary monodentate ligand, have been intensively studied as chemical sensors, photosensitisers for solar energy conversion and bioimaging and luminescent probes.[2] In the latter case, the luminescence properties of these complexes were directly connected to the nature of the auxiliary monodentate ligand L. The tunability of this "2+1 complexation" approach around a tricarbonyl rhenium(I) core is still of great interest. Recently, Faulkner's group reported an elegant synthesis of a bimetallic complex containing a luminescent rhenium chromophore as well as a Gd^{3+} ion that can be used in magnetic resonance imaging (MRI). In this single-molecule dual imaging agent, the rhenium tricarbonyl core is surrounded both by a 2,2′-bipyridine moiety and a pyridine group connected to a Gd^{3+} DOTA complex.[3]

Most reported luminescent rhenium(I) tricarbonyl complexes are confined to systems containing nonfunctionalised 2,2′-bipyridine, preventing their use as target-specific imaging probes. The preparation of such monofunctionalised chelators, which still requires multiple-step syntheses and/or fastidious purification steps, generally suffers from low overall yields. Particular interest has been recently devoted to the "click synthesis" of monofunctionalised 2-pyridyl-1,2,3-triazole derivatives (or pyta) as alternative ligands to 2,2′-bipyridines. The mild reaction conditions associated with the click approach allowed the preparation of a large number of monofunctionalised pyta derivatives.[4] Nevertheless, only a few of them possess a tethering group for further coupling to a biomolecule.[4c]

In this regard, we report here an extension of this click synthetic strategy with the design and convenient synthesis of a new pyta-based bifunctional chelating agent. The preparation of 2-pyridyl-1,2,3-triazole derivatives bearing a -COOR arm (Scheme 1), as well as the investigation of their coordinating abilities with a tricarbonyl rhenium core, is presented herein. Surprisingly, depending on the nature of the R group, different rhenium complexes have been obtained – ranging from classical mononuclear complexes to a mixture of two structural isomers of unconventional tricarbonyl rhenium(I) dimeric species. Definitive characterisation of the latter compounds was accomplished by X-ray crystallography and DFT calculations.

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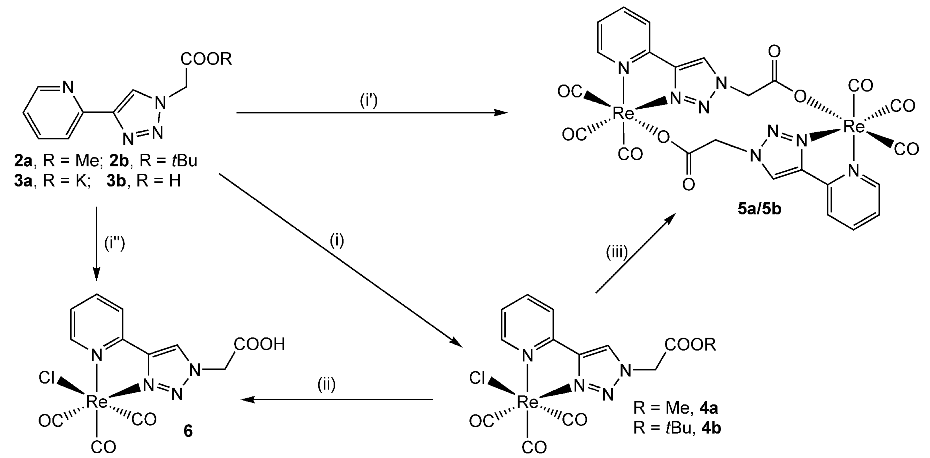


Scheme 1. Synthesis and structures of Re(CO)$_3$ complexes. Conditions and reagents: (i) **2a** or **2b**, Re(CO)$_5$Cl, MeOH, 65 °C, overnight, 79–87%, (i′) **3a**, Re(CO)$_5$Cl, MeOH, 65 °C, overnight, 66%, (i′′) **3b**, Re(CO)$_5$Cl, MeOH, 65 °C, overnight, 50% (ii) **4b**, TFA/CH$_2$Cl$_2$ (15:1, v/v), room temp., overnight, 82%, (iii) **4a**, K$_2$CO$_3$, MeOH/H$_2$O, room temp., overnight, 47%.

Results and Discussion

By applying classical click conditions[5] – copper(I) catalyst, room temperature, *t*BuOH/water mixture (1:1 v/v) – the alkyl 2-[4-(2-pyridyl-1,2,3-triazol-1-yl)]acetate scaffolds **2a** and **2b** were easily synthesised in high yields from methyl or *tert*-butyl azidoacetate and commercial ethynylpyridine. Compounds **3a** or **3b** were obtained after basic or acidic hydrolysis of the ester pendant arm at room temperature, respectively. The convenient preparation of these latter compounds contrasts with the methodology reported recently for the synthesis of an analogous pyta ligand (microwave, 100–125 °C, 21% yield) bearing a carboxylic acid arm.[4c]

These monofunctionalised pyridyl-1,2,3-triazole derivatives were fully characterised by classical spectroscopic methods (see Supporting Information). It is worth noting that colourless crystals of **2a** were obtained by slow evaporation of a dichloromethane/methanol solution.[6] A representation of the structure appears in Figure 1. Structural features are very similar and compare well to those observed for related complexes, that is, an *anti* arrangement adopted by the N1 and N2 atoms of the pyridine and triazole rings, respectively, and an azo character of the 1,2,3-triazole ring.[4a,4d–4f] Interestingly, a significant contribution to crystal cohesion is provided by a network of intralayer hydrogen bonds in which the ligand and two lattice water molecules participate. Each lattice water molecule forms O–H···N bonds with the pyridine or triazole nitrogen atoms of the ligand molecule. At the same time, each lattice water molecule acts both as the acceptor and the donor in O–H···O hydrogen bonds of another lattice water molecule (see Supporting Information).

Scheme 1 highlights the preparative strategies employed for the rhenium complexes. As expected, mononuclear complexes [ReCl(CO)$_3$(pyta-COOR)] (R = Me; **4a**) or (R = *t*Bu; **4b**) were obtained in good yield (79–87%) from the reaction between Re(CO)$_5$Cl and **2a** or **2b** in methanol heated at reflux. The elemental analysis, NMR (^{1}H-^{1}H and ^{1}H-^{13}C experiments) and IR spectroscopy and mass spectrometry data are completely consistent with the above formulation as mononuclear tricarbonyl rhenium(I) species. The pattern of the C–O stretching frequencies in the IR spectra, of one sharp, intense absorption at approximately 2025 cm^{-1} and a second broad, intense band in the 1890–1915 cm^{-1} region, confirms the facial arrangement of the CO ligands in the complexes. In the mass spectra, the prominent peak observed at m/z = 565 for **4a** and m/z = 582 for **4b** is assigned to [M + NH$_4^+$]$^+$ on the basis of the isotopic distribution of $^{185/187}$Re. Then, in the ^{1}H NMR spectra, the triazole proton signals were strongly shifted downfield (0.2 to 0.9 ppm) relative to those of the pyta ligands. Additionally, these spectroscopic assignments were confirmed by the solid-state structure of **4a** elucidated by X-ray crystallography (see Supporting Information for details).[7] As commonly

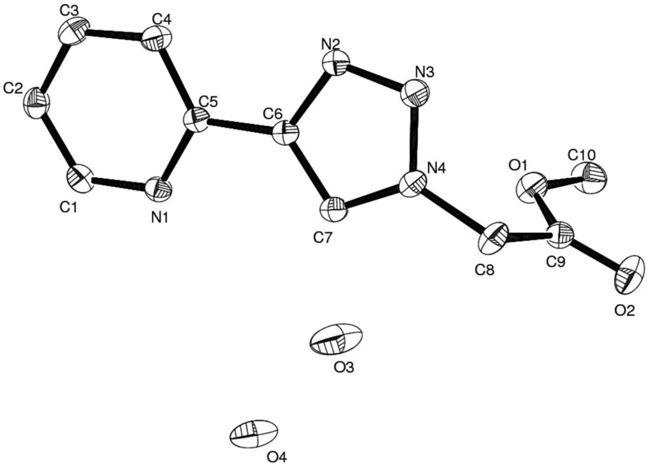


Figure 1. Labelled ORTEP diagram of (pyta-COOMe)·2H$_2$O (**2a**·2H$_2$O) with thermal ellipsoids shown at 30% probability. Hydrogen atoms are omitted for clarity. Selected distances [Å] and angles [°]: N2–N3 1.313(2), N3–N4 1.346(2), C7–C6 1.377(2), C6–N2 1.370(2), C6–C5 1.471(2), C6–N2–N3 109.22(13), N2–N3–N4 106.83(13), N3–N4–C7 111.48(13), C6–C5–N1 116.55(14), C5–C6–N2 121.71(14).

found for tricarbonyl rhenium(I) complexes, the rhenium(I) centre presents a distorted octahedral geometry. In the "ReC3N2Cl" coordination sphere, the three carbon monoxide moieties are facially disposed to maximise Re–CO backbonding. The chelate ring is satisfactorily planar, with unexceptional bond lengths and bond angles that are close to those observed in similar $Re(CO)_3$ pyta complexes.[4e] In particular, the N2–N3 distance is slightly longer in the complex relative to that in the free ligand [1.322(9) vs. 1.313(2) Å], this structural feature being consistent with the back donation from the metal centre to the triazole ring.[4d] Since the ester arm remains uncoordinated, it should offer, after conversion into a carboxylic acid group, an ideal site for further bioconjugation. The corresponding pyta **6** bearing a carboxylic acid arm has been obtained by acid hydrolysis of the *t*Bu group of **4b** or by the complexation reaction of **3b** with $Re(CO)_5Cl$ in methanol heated at reflux. The modest 50% yield of the latter procedure could be explained by the in situ esterification of the acidic function resulting in approximately 20% yield for **4a** as identified by NMR spectroscopy and mass spectra.

Unexpectedly, neither the complexation of **3a** under the same complexation conditions as above nor the basic hydrolysis of the methyl ester pendant arm of complex **4a** lead to **6**. Instead, a mixture of tricarbonyl rhenium(I) dimeric species **5a/5b**, in a 3:1 ratio, resulting from cyclisation of two mononuclear complexes, the chlorine atom of the labile Re–Cl bond of one monomer being substituted by the oxygen of the carboxylate arm of the second one (Scheme 1), was obtained. In the IR spectrum, the presence of three very strong ν(CO) bands in the range 2020–1883 cm^{-1} confirmed the *fac* geometry around the rhenium atoms. In the ^1H NMR spectrum, the methylene protons close to the carboxylate group exhibited a set of doublets corresponding to AB-spin systems in the region 4.90–5.16 ppm with geminal coupling constants of approximately 17.0 Hz. The magnetic inequivalence of such CH_2 protons highlights the coordination of the carboxylate arms to the rhenium centres.[8] Despite the low solubility of the product (only soluble in DMF and DMSO), a HPLC/MS analysis was performed, and two peaks in an approximately 3:1 ratio were observed. Their FAB spectra displayed signals corresponding to the dimer $[Re(CO)_3(pyta\text{-}COO)]_2$ and no signals with higher *m*/*z* values. Under the same conditions, a semipreparative HPLC purification was achieved, but only the major isomer **5a** was obtained in pure form in the milligram scale. The solid-state structure obtained for this compound provided further evidence for the formation of these unusual dinuclear metallacycles (Figure 2 and Supporting Information).

The rhenium atoms are octahedrally coordinated to three carbonyl groups in *fac* arrangement and two nitrogen atoms of one pyta moiety and an oxygen atom of the other. Interestingly, the Re–carbonyl bond lengths are the shortest in the $Re(CO)_3$ complexes based on pyta moieties (mean length 1.90–1.91 Å for **5a** vs. 1.92 Å for **4a** and 1.92–1.94 Å for an analogous complex[4f]). As to the Re–O distances (2.115–2.136 Å), they are close to those found in related compounds in which a carboxylate oxygen is coordinated *trans* to a carbonyl ligand. The rather large deviations from the idealised octahedral geometry (bond angle ranges: *cis* 78.2–97.2°; *trans*, 171.5–173.5°) can be ascribed to the constraints imposed by ring closure, the N–Re–N bite angles being approximately 74.5°. Even if the centroid–centroid distance of the triazole rings (4.321 Å) is not representative of π–π stacking,[9] this weak interaction probably makes a significant contribution to the stability of the dimeric structure. Moreover, the stability of **5a** and the structure elucidation of the second isomer have been confirmed from a theoretical point of view.

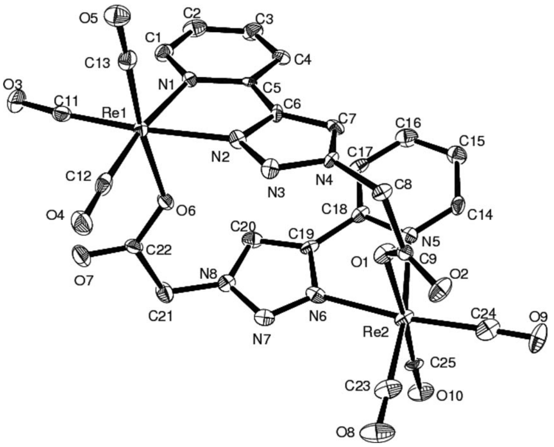
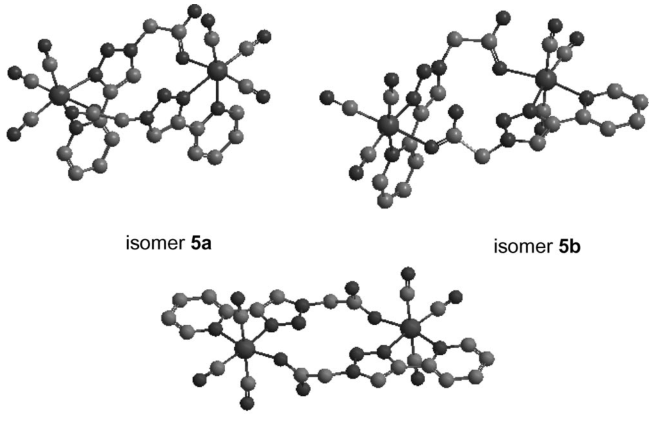


Figure 2. Molecular view of complex **5a** in the solid state, with thermal ellipsoids shown at 30% probability. Hydrogen atoms are omitted for clarity. Selected distances [Å] and angles [°]: N1–Re1 2.208(6), N2–Re1 2.152(7), Re1–O6 2.136(6), Re1–C11 1.914(10), Re1–C12 1.896(10), Re1–C13 1.891(11), N5–Re2 2.214(7), N6–Re2 2.145(8), Re2–O1 2.115(6), Re2–C23 1.922(10), Re2–C24 1.928(11), Re2–C25 1.884(10), N1–Re1–C12 172.1(3), N2–Re1–C11 170.3(3), N1–Re1–O6 80.6(2), N5–Re2–C23 171.5(4), N6–Re2–C24 173.4(3), N5–Re2–O1 78.2(2).

DFT calculations[10] were carried out on the potential structures of the dimer. Three different isomers were optimised and found to be minima on the potential energy surface (PES) (Figure 3). The most stable isomer is complex **5a**, in which the two pyta ligands are in two parallel planes. The geometry obtained theoretically is in good agreement with that obtained by X-ray crystallography and with the spectroscopic data. In particular, the chemical shift of the proton of the triazole moieties is well reproduced (calculated value of 7.10 ppm to be compared with an experimental value of 8.08 ppm for the major product). The second isomer, **5b**, is found to be less stable than isomer **5a** (by 21.7 $kcal\,mol^{-1}$). This free energy difference at room temperature indicates that this isomer can only be a minor product. In this isomer, the two pyta ligands are in two different planes but are perpendicular to each other. The ^1H NMR chemical shift for the triazole proton signal is calculated as 8.05 ppm (higher field than that for isomer **5a**), in agreement with the experimental observation for the second isomer (9.00 ppm). The last isomer, **5c**, is much higher in energy (46.7 kcal mol^{-1} relative to isomer **5a**) and cannot account for any spectroscopic signature in this experiment.


isomer **5a**

isomer **5b**

isomer **5c**

Figure 3. Optimised structures of the three different isomers.

Although tetrameric or trimeric $Re(CO)_3$ species have been widely reported in the literature with, for example, ligands containing pyridine functionalities on opposite ends of an organic linker,[11] or thiosemicarbazone ligands,[12] the formation of $Re(CO)_3$ dimeric species in good yield is still very rare.[12b] The nature of the ligands has a tremendous impact on the size of the formed oligomers. In the case of thiosemicarbazone ligands, tetramers were predominantly obtained with rigid ligands, while trimers were formed by more flexible ones. In our case, only dimers were obtained in fair yield – ranging from 47 to 66%. The planarity/rigidity of the heteroaromatic skeleton conjugated to a very flexible coordinating arm could explain the easy formation of **5**, the driving force being that the cyclisation of two monomers gives very stable dinuclear metallacycles. Attempts to substitute the chlorine in the Re–Cl bond of compounds **4a** or **4b** by aliphatic carboxylate derivatives such as $CH_3(CH_2)_n$-COO^- (n = 3 to 5) failed completely, even after two days in methanol heated at reflux. The process reported here has no precedent in the literature, since to the best of our knowledge the only reported example involves a rhenium dinuclear metallacycle synthesised from a 3,3′-difunctionalised bipyridine (3,3′-dcbpy), obtained as a side-product in very low yield.[13] In contrast to this previously reported dinuclear complex, dimer **5** and monomer **4a** or **4b** exhibit fluorescence at room temperature in 8:2 MeOH/DMF solution (see Supporting Information). Spectra were very similar to those of analogous Re^I tricarbonyl diimine complexes, the compounds displaying strong absorption bands at approximately 260–318 nm and a less intense absorption shoulder at approximately 320–380 nm, assigned to ligand-centred (LC) [$\pi \rightarrow \pi^*$] and metal-to-ligand charge-transfer (MLCT) [$d\pi(Re) \rightarrow \pi^*(pyta)$] transitions, respectively.[4e] The observed quantum yield for dimer **5** (Φ = 0.55%) is much higher (by a factor of about 2) than those for **4a** or $[ReCl(CO)_3bipy]$ used as reference (Table 1).[14] Interestingly, this value is similar to those observed for Re^I complexes of the type $[Re(bipy)(CO)_3L]$ (L = substituted pyridine).[15]

Table 1. Electronic, emission spectroscopic data and quantum yields (Φ) in DMF/MeOH solution for $[ReCl(CO)_3bipy]$, **4a** and **5** at 298 K.

Compound	UV/Vis data λ_{max} [nm] (ε [$M^{-1}cm^{-1}$])	λ_{em} [nm][a]	Φ
$[ReCl(CO)_3bipy]$	294 (14938), 317 (10032), 371 (3808)	598	0.0023
4	271 (9213), 333 (3341)	526	0.0029
5	267 (24787), 291 (18837), 326 (9160)	526	0.0055

[a] Excitation at the absorption peak in the region 326–371 nm.

Conclusions

In conclusion, new pyta-based bifunctional chelating agents as well as their corresponding luminescent rhenium(I) complexes can be prepared easily, in excellent yield, by click chemistry. We deem the unexpected formation of **5** particularly attractive, as it opens new horizons in the coordination chemistry of the $Re(CO)_3^+$ core and it represents an original and effective strategy toward the synthesis of new luminescent rhenium(I) dimeric (multimeric) species. Further studies in this direction are underway with various pyta ligands bearing carboxylic acid arms.

Experimental Section

Please see the Supporting Information for detailed information on general experimental details for the syntheses and selected data for characterisation of the ligands and rhenium complexes.

CCDC-779387 (compound **2a**), -779388 (compound **4a**), and -779389 (compound **5a**) 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.

Supporting Information (see footnote on the first page of this article): Experimental details, characterisation data, X-ray structures, spectroscopic data and DFT calculations.

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[7] The scattering data for **4a** show disordered solvent molecules difficult to model; consequently, the SQUEEZE program from PLATON (P. Vandersluis, A. L. Speck, *Acta Crystallogr., Sect. A* **1990**, *46*, 194–201), was used to correct the data. Crystal data for [ReCl(CO)$_3$(pyta-COOMe)] **4a**: M = 523.91, monoclinic, space group $P2_1/c$, a = 7.8606(2) Å, b = 11.6177(3) Å, c = 21.5808(6) Å, V = 1952.91(9) Å^3, T = 193(2) K, Z = 4, 18123 reflections measured (3569 independent, R_{int} = 0.0505), 218 parameters, R_1 [$I > 2\sigma(I)$] = 0.04, *wR2* [all data] = 0.1008, largest diff. peak and hole: 2.064 and –0.819 e A^{-3}.

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