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Manganese Carbonyl Terpyridyl Complexes. Their Synthesis, Characterization and Potential Application as CO-Release Molecules.

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**Mn[I] carbonyl terpyridyl complexes have been synthesized and characterized. The tricarbonyl derivative exhibits interesting behaviors for controlled CO-release by both thermal and photosynthetic pathways.**

Metal carbonyl complexes incorporating nitrogen heterocyclic ligands, especially those based on rhenium like for instance $[Re^I(L)(CO)_3X]$ (L = bidentate diimine ligand), have been the subject of extensive investigation for applications ranging from the photo or electrocatalysis of CO_2 reduction[1] to the design of new active CO-release molecules (CO-RMs) as therapeutic agents.[2] The interest in these compounds stems from their various physico-chemical properties which depend largely on the ligand structure. Less is known about dicarbonyl Re equivalent complexes.[3] The strategy of developing studies looking at the effects of the ligand structure and the nature of metals in this type of complex greatly expands the range of properties and thus enhances their potential applications. Considering the general trend of replacing unsustainable noble metals by abundant first-row transition metals, manganese complexes are more and more envisioned as promising and safe substitutes to their Re counterparts. Whereas a significant number of Mn-carbonyl complexes are already known as CO-RMs,[2,4] our group[5] and C. P. Kubiak's [6] have recently demonstrated that complexes like $[Mn(bipyridyl)(CO)_3Br]$ could be used as selective electrocatalysts for CO_2 reduction, as efficient as their Re tricarbonyl analogues. As a continuation of our interest in exploring Mn[I]-carbonyl-polypyridyl complexes, in order to find new molecules for catalysis or CO-RM applications, we have prepared novel Mn[I] complexes featuring the ambidente 2,2':6',2"-terpyridine (terpy) ligand (Scheme 1). We expected that an incoming pre-organized ligand close to the metal in the tri-CO terpy-κ^2N^1,N^2 Mn complex **1b**, would help the decoordination of a CO ligand and lead to the di-CO terpy-κ^3N^1,N^2,N^3 species **2**. Such decarbonylation reaction is essential for both electrocatalysis of CO_2 reduction and CO-release reactions utilizing carbonyl metallic complexes. The effect induced by a pre-organized chelating group close to the metallic center, on CO photodissociation reaction, has been recently demonstrated for cyclopentadienyl Mn-tricarbonyl derivatives.[7] It should be underlined that $[Re(terpy-\kappa^2N^1,N^2)(CO)_3Cl]$ was reported in the 90s,[8a-b] and the dicarbonyl corresponding species was synthesized

only recently by a thermal CO substitution under very harsh conditions[8c] but, as far as we know, never by a photochemical pathway.

Herein we report both synthetic pathways, which we have developed to synthesize **1a** and **1b** and to convert **1b** into **2** by CO substitution reactions in mild experimental conditions, as well as their characterizations and potential applications.

1a: X = Br   n = 0
1b: X = NCMe n = 1

2: X = NCMe n = 1
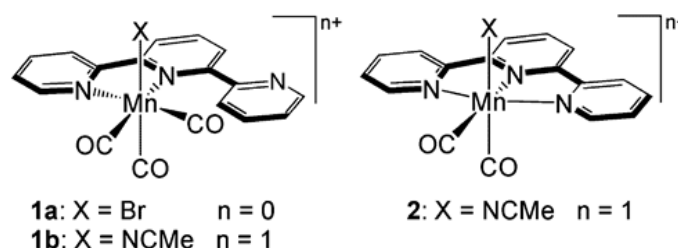
Scheme 1 The synthesized terpyridyl complexes.

fac-$[Mn(terpy-\kappa^2N^1,N^2)(CO)_3Br]$ (**1a**), in which the terpy is acting as a bidentate ligand (NN-chelate), was synthesized with almost 90% yield from $[Mn(CO)_5Br]$ (see ESI† for experimental details and full characterizations). The FTIR spectrum of **1a** features three distinct $\nu_{C\equiv O}$ stretching bands, in agreement with those observed in other fac-Mn tricarbonyl complexes.[9] ^{1}H and ^{13}C NMR spectra are characteristic of an unsymmetrically coordinated terpy. Single crystals of **1a** (yellow blocks) have been grown by slow vapor diffusion of diisopropyl ether in a DMF solution. The crystallographic structure‡ shows both enantiomers of **1a** coexist in the unit cell, which is thus racemic. The asymmetric unit is presented on Fig. 1; it confirms the fac configuration of the complex and the bidentate coordination mode of the terpy to the Mn center, leaving one of the outer pyridyl rings uncoordinated (see Fig.S1 and Table S1 in ESI† for crystal data, atoms numbering and characteristic bond lengths). The dihedral angle between the two coordinated pyridyl rings is 16.5°, between the middle ring and the non-coordinated ring 143.2°, a distortion which is higher than the one observed in the Re analogue $[Re(terpy-\kappa^2N^1,N^2)(CO)_3Cl]$ (6.9° and 130.0°, respectively).[10] The non-coplanarity of the free pyridyl is obviously due to steric hindrance of the neighboring CO ligand.
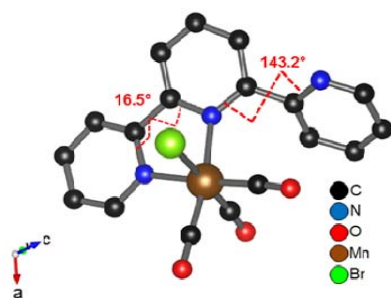
Fig. 1 Ball-and-stick representation of the asymmetric unit in **1a**.

1a solubilizes well in MeCN, where the bromide is gradually exchanged for an MeCN molecule, but this substitution is incomplete and slow (Fig. S2 in ESI†). Thereby, [Mn(terpy-κ^2N^1,N^2)(CO)$_3$(MeCN)](PF$_6$) (**1b**) has been quantitatively prepared by reaction of **1a** with AgPF$_6$. **1b** is soluble in MeCN, and moderately soluble in H$_2$O (saturation concentration $\approx$ 0.5 mM). When dissolved in MeCN, it shows two strong absorption bands in the UV region at λ_{max} = 280 and 296 nm (ε = 1.4×10^4 M^{-1} cm^{-1} for both), attributed to intra-ligand (IL) transitions (π-π^* terpy) in accordance with those observed for Re-terpyridyl tri-CO analogues.[8a] A single, weaker band is observed in the visible region, at λ_{max} = 370 nm (ε = 2800 M^{-1} cm^{-1}); it has been attributed to a metal-to-ligand charge transfer (MLCT).[9a] In water, this latter is red-shifted (λ_{max} = 390 nm), presumably due to the exchange of the coordinated MeCN by H$_2$O. No change in the UV-Vis spectra was observed after leaving the solutions for 24 h in the dark, confirming the good stability of **1b** for an extended period of time in both organic and aqueous media. However, selective photolysis (λ_{irr} = 372 nm) of a MeCN solution of **1b** quickly leads to the apparition of two new broad absorption bands, centered at 460 and 610 nm. Those are characteristic of *mer,cis*-[Mn(terpy-κ^3N^1,N^2,N^3)(CO)$_2$(MeCN)]$^+$ dicarbonyl complex (**2**), where one CO is replaced by the initially non-coordinated pyridyl of the terpy ligand (Equation(1)). Similar photoconversion has been proposed for instance for *fac*-[Mn(iPr-DAB)(CO)$_3$Br],[11] and for a trispyridyl amine Re complex,[8b] but, as far as we know, never for the Re-terpy-κ^2N^1,N^2 equivalent compound.

$$[Mn(terpy-\kappa^2N^1,N^2)(CO)_3(MeCN)]^+ \rightarrow$$
$$[Mn(terpy-\kappa^3N^1,N^2,N^3)(CO)_2(MeCN)]^+ + CO \qquad (1)$$
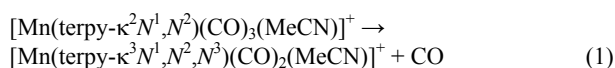
To characterize **2** more accurately we have developed a synthetic pathway, alternative to the photo-activated loss of CO, by refluxing an acetonitrile solution of **1b**, in the absence of light; however this reaction is quite slow ($\approx$ 20% conversion after 4 h). The kinetics of this process has been improved by keeping the solution of **1b** under reduced pressure, in a H$_2$O/MeCN mixture, for a few hours. The progress of this decarbonylation reaction was monitored by ^{1}H and ^{13}C NMR. Representative spectra on Fig. 2 show the disappearance of the characteristic signals of the bidentate terpy-κ^2N^1,N^2 in **1b**, and the concomitant apparition of the six signals of the symmetrical tridentate terpy-κ^3N^1,N^2,N^3 in **2**. The reaction is quantitative, no intermediate species was ever observed in these conditions. Similarly, the ^{13}C spectrum of **2** exhibits in the 100–180 ppm region the eight peaks expected from a symmetrical tridentate terpy, as opposed to the fifteen distinct peaks of terpy in **1b**. Moreover, the IR spectrum of **2** differs strongly from the one of its parent complex, with an important shift of the C≡O stretching bands towards lower wavenumbers (Fig. S3a in ESI†); the new pattern is consistent with two CO ligands in *cis* configuration as it was previously observed for [Re(tris-(2-pyridyl)-amine)(CO)$_2$Cl].[8b]
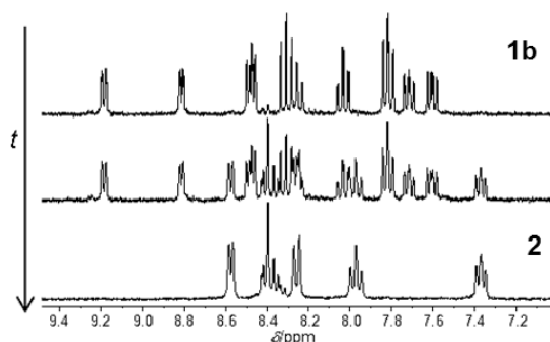

Fig. 2 Representative ^{1}H NMR spectra (CD$_3$CN) in the aromatic region following the evolution of a solution of **1b** when warmed under vacuum, showing the conversion of **1b** into **2**.

The UV-Vis spectrum of **2** in MeCN is characterized by three strong absorption bands in the UV region at λ_{max} = 229, 280 and 323 nm (ε = 2.5, 1.6 and 2.0 ×10^4 M^{-1} cm^{-1}, respectively), attributed to π-π^* intra-ligand (IL) transitions, and three weaker ones at λ_{max} = 380, 456 and 617 nm (ε = 2200, 2400 and 870 M^{-1} cm^{-1}, respectively; Fig.S4 in ESI†), confirming the products formed by photo- and thermal dissociation of **1b** are the same. The changes in the IL bands may be explained by the change in the terpy distortion between **1b** and **2**.

The photochemical properties of **1b** have been monitored by UV-vis (Fig. 3), IR, and ^{1}H NMR (Fig. S3 and S5 in ESI†) spectroscopies in MeCN. Under inert atmosphere, the mono-decarbonylation process is clean, quantitative and occurs with a good quantum yield (ϕ = 0.7). This yield was determined by chemical actinometry using a solution of a dicarbonyl Ru complex as an external standard (ϕ_{ref} = 1, see ESI†).[12] To prove the advantages in using an ambidente terpy ligand instead of a bidentate bpy one, we have investigated *fac*-[Mn(bpy)(CO)$_3$(MeCN)](PF$_6$) irradiation in MeCN. The quantitative mono-decarbonylation of the bpy complex could not be achieved since the di- and tri-decarbonylation take place before the mono-decarbonylation is complete. We have compared the rate of the mono-decarbonylation process for **1b** and the bpy equivalent species, in the exact same experimental irradiation conditions, and have shown that this rate is roughly twice as fast for **1b**; this is likely due to the chelating effect of the free pyridyl of the terpy-κ^2N^1,N^2 close to the Mn^I center in **1b**. Addition of even a large excess of pyridine in the solution of [Mn(bpy)(CO)$_3$(MeCN)](PF$_6$) does not affect the decarbonylation.

Maintaining the irradiation of **1b** at λ_{irr} = 372 nm past the first step (Equation (1)) led to the complete decarbonylation and the formation of [Mn(terpy)$_2$]$^{2+}$, identified by IR, EPR and electrochemistry, as well as yet unknown byproducts. Overall, this process is around ten times slower than the first monodecarbonylation step. Gas chromatography (GC) analysis of the gas phase has allowed a precise detection and quantification of CO: one molar equivalent of CO is released concomitantly to the formation of **2**, and two further equivalents when the irradiation is carried on beyond this point. Besides, an important feature is the possibility of interrupting the monodecarbonylation reaction at any time, by simply switching off the irradiation (Fig. 3 inset); this can be repeated as often as needed, allowing a precisely controlled CO release, a crucial point for potential activated CO-RM applications. When kept in the dark, a deaerated solution of **2** is stable for days. The reaction outcome is altered significantly in the presence of O$_2$. Under aerobic conditions, the maximum conversion of **1b** into **2** which could ever be reached has been around 60%, with further irradiation leading to the concurrent decarbonylation of **2**, revealed by a decrease of all the absorption bands on the UV-Vis spectrum. This is in agreement with
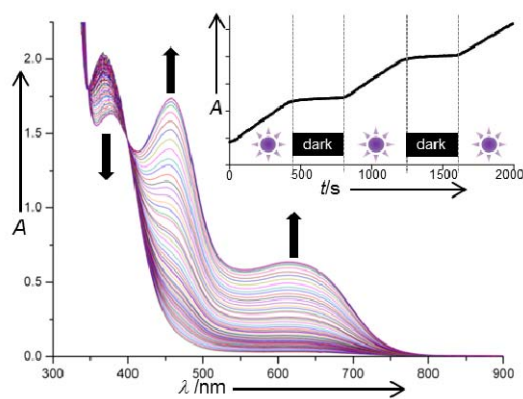
Fig. 3 UV-Vis spectra of a solution of **1b** in acetonitrile (C=0.68 mM) under irradiation at λ_{irr} = 372 nm, under Ar. One spectrum recorded every 20 s, l = 1 cm. Inset: evolution of the absorbance at λ = 456 nm during cycles where irradiation is alternately switched on and off.

an observation described recently by Kurz *et al.*[13] They have spectroscopically demonstrated that complexes such as [Mn(tpm)(CO)$_3$] (tpm = tris(pyrazolyl)methane) first lose one CO by irradiation, and then the last two CO in a reaction accompanied by oxidation of the Mn^{I} center by O$_2$. Following the photo-reaction of **1b** in pure water is trickier, due to the very low solubility of the photogenerated product in this medium, which prevents an accurate UV-Vis study. However at the beginning of the reaction, we have clearly demonstrated that the decarbonylation process in water is similar to what was observed in an organic medium (Fig. S6 in ESI†). Eventually, in both organic and aqueous media, exposure to white light leads to complete decarbonylation in a few minutes.

The complexes have been further characterized by electrochemistry, all the measurements being conducted in the dark in a MeCN electrolyte. On the initial reduction scan, the cyclic voltammograms (CVs) of **1b** and **2** (Fig. S7 in ESI†) show two successive irreversible reductions at the same potentials (E_{pc1} = -1.46 V and E_{pc2} = -1.68 V vs. Ag/Ag^{+}). On the oxidation side however CVs of **1b** and **2** differ clearly, the latter being irreversibly oxidized much more easily (E_{pa} = 0.28 V) than the former (E_{pa} = 0.98 V), explaining the greater instability of **2** in non-deoxygenated solutions. The complete electrochemical study of these Mn-terpy complexes is under way and will be detailed elsewhere.

To conclude, we have described the first quantitative synthesis of di and tricarbonyl Mn-terpy complexes and their characterizations. Besides the synthetic aspect, the study of the photo-activation of CO release in the tricarbonyl Mn^{I} terpy compound has shown the role of the ambidentate terpy ligand on the rate of the CO-release reaction. The latter species is able to respond to an external controlled trigger (UV irradiation), in both organic and aqueous media, which could be suitable for CO-based therapeutics. Preliminary qualitative analysis of CO$_2$ reduction activation conducted with Mn-terpy carbonyl complexes in hydro-organic electrolytes (Fig. S8 in ESI†) has shown the potential of this Mn-based derivatives as homogeneous molecular electrocatalysts. We are currently studying in detail the redox reactions and how various substituents on the terpy ligand may influence the efficiency of the processes of CO-release and also of CO$_2$ electrocatalytic reduction.

Notes and references

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† Electronic Supplementary Information (ESI) available: detailed experimental procedures, further characterizations, and crystallographic data. See DOI: 10.1039/c000000x/
‡ CCDC 961705 contains 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.

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