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M-CPOnes: transition metal complexes with cyclopropenone-based ligands for light-triggered carbon monoxide release†

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A new class of CO-releasing molecules, M-CPOnes, was prepared combining cyclopropenone-based ligands for CO release with the modular scaffold of transition metal complexes. In proof-of-concept studies, M-CPOnes based on Zn^{II}, Fe^{II} and Co^{II} are stable in the dark but undergo light-triggered CO release with the cyclopropenone substituents and metal ions enabling tuning of the photophysical properties. Furthermore, the choice of metal allows the use of different spectroscopic methods to monitor photodecarbonylation from fluorescence spectroscopy to UV/vis spectroscopy and paramagnetic NMR spectroscopy. The modularity of M-CPOnes from the metal ion to the cyclopropenone substitution and potential for further functionalisation of the ligand make M-CPOnes appealing for tailored functionality in applications.

Introduction

Carbon monoxide has potential therapeutic applications,[1] *e.g.* for treatment of inflammation and vascular dysfunction,[2–5] given the role of carbon monoxide in the regulation of ion channels[6,7] and signalling pathways.[8,9] Since the safe handling and delivery of gaseous carbon monoxide is problematic, carbon monoxide releasing molecules (CORMs)[3] have been developed for the controlled release of carbon monoxide in response to stimuli. These include metal carbonyl complexes[10] (such as tricarbonyldichlororuthenium(II) dimer (CORM-2),[11] (tricarbonylchloro(glycinato)ruthenium (CORM-3)[12]), non-metallic/organic CORMs[13] and carbon monoxide "prodrugs".[14,15] For applications, the CORM should have good stability but triggerable and quantitative CO release as well as tunable photophysical properties and synthetic accessibility.[16]

Photo-CORMs[17–20] take advantage of the spatial and temporal control of light to release carbon monoxide upon irradiation[16,21] and in some cases, the loss of carbon monoxide could be tracked by fluorescence.[22–24] While cyclopropenones[25,26] undergo efficient photolysis[27,28] upon irradiation with light resulting in carbon monoxide release and alkyne formation, they have been largely overlooked as CORMs.[16] Instead, cyclopropenones have found use across different fields from organic chemistry (as substrates in annulations,[29–33] metal-catalysed ring-opening reactions,[34] cycloaddition reactions[35,36] and allene syntheses[37,38] as well as catalysts for nucleophilic substitutions[39,40]) to material science[18,41,42] and biorthogonal chemistry.[43–48]

Cyclopropenones are appealing as prospective CORMs not only for their efficient photodecarbonylation but since they can be prepared *via* various synthetic methods (*e.g.* Friedel–Crafts reaction,[49–53] [2 + 1] cycloaddition and hydrolysis,[37,54–57] Favorskii rearrangement[29,39,58,59] and substitution of cyclopropenone acetals[60–63]). In addition, they are stable in aqueous media and cellular environments[45,47,64] and there is the potential to exploit multi-photon induced decarbonylation for carbon monoxide release at higher wavelengths (800–950 nm).[65,66]

We envisaged the combination of cyclopropenones with transition metal complexes could lead to a new class of CO-releasing molecules, M-CPOnes (Scheme 1), as an alternative to metal carbonyl complexes; light could be exploited as a reagent-free trigger for CO release from the cyclopropenone while the transition metal complex could serve as a modular scaffold for not only introducing multiple cyclopropenone moieties but also tuning properties such as the stability, solubility and photodecarbonylation wavelength through the choice of metal and ligands.

We report cyclopropenone ligands based on a 2,2′-bipyridine coordination motif are now synthetically accessible *via* a cycloaddition and subsequent hydrolysis and in addition, their photophysical properties are tunable through the R substitu-

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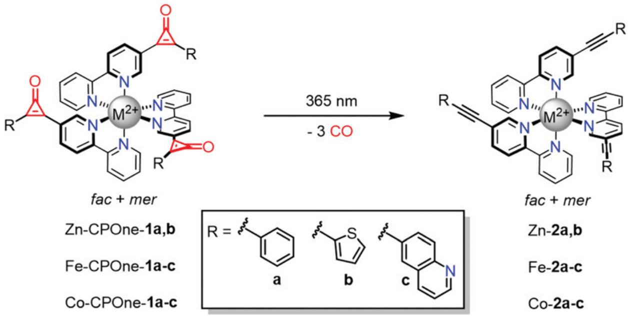
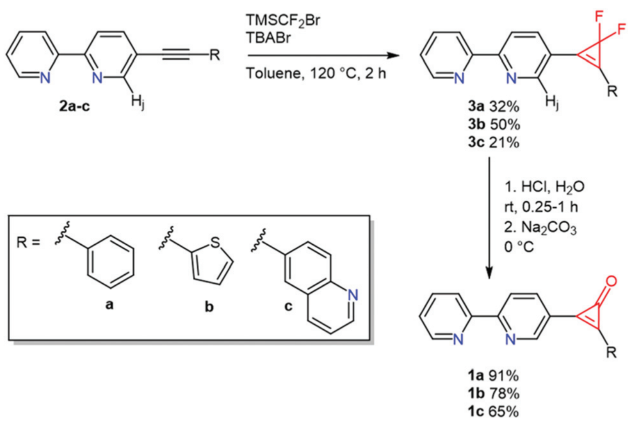


Scheme 1 Proof-of-concept of M-CPOnes: light triggered CO release from transition metal complexes with cyclopropenone-based ligands. The complexes form as a mixture of the *fac* and *mer* isomers but only the *fac* isomer is depicted for clarity.

ent. The M-CPOnes resulting from complexation with Zn^{II}, Fe^{II} and Co^{II} metal ions are stable in the dark but undergo photodecarbonylation upon irradiation with 365 nm light (Scheme 1). Thus, we demonstrate the proof-of-concept of M-CPOnes as a new class of CO-releasing molecules and this lays the groundwork for future investigation of their application as CORMs.

Results and discussion

Given diphenylcyclopropenone is one of the simplest and most well-studied diaryl-substituted cyclopropenones,[67–69] the initial target ligand was **1a** (Scheme 2) where one of the phenyl groups was replaced with a simple 2,2′-bipyridine as the coordination motif for the development of this new class of CO-releasing molecules, M-CPOnes. Furthermore, ligands **1b** and **1c** would also be prepared where the second substituent was varied from a phenyl group to an electron rich thienyl and second N-heterocyclic substituent, respectively, to study the electronic effects of the aryl substituents on the stability and photophysical properties of the cyclopropenones and their corresponding M-CPOnes (Scheme 1).



Scheme 2 Synthesis of N-heterocyclic cyclopropenones **1a-c** *via* a [2 + 1] cycloaddition of :CF_2 with alkyne derivatives **2a-c** and subsequent hydrolysis of the corresponding difluorocyclopropenes **3a-c**.

While there are numerous examples of alkyl- and carbocyclic aryl-substituted cyclopropenones,[25–29,39,41,45,47,58,59,62,63,65,66,70–72] heterocyclic-based cyclopropenones are relatively rare[73] and typically based on more electron-rich 5-membered heterocycles.[37,74,75] Due to the incompatibility of Lewis acid reagents like $AlCl_3$ with the 2,2′-bipyridine coordination motif in the commonly employed synthesis of cyclopropenones *via* a Friedel–Crafts reaction,[76] we focused on an alternative synthetic strategy involving a [2 + 1] cycloaddition between a dihalocarbene[77,78] and acetylene derivative followed by hydrolysis of the dihalocyclopropene (Scheme 2).

Even though the synthesis of difluorocyclopropenes *via* a cycloaddition is, in general, well established,[78–80] there are a scarcity of examples of electron-deficient N-heterocyclic difluorocyclopropenes. We expected the cycloaddition to be challenging given the more electron-deficient nature of the substrates and since Lewis bases such as pyridine have been proposed to coordinate to the :CF_2 during the cycloaddition causing decomposition or difluoromethylation.[77,78,81–84] We hypothesised the reduced basicity of 2,2′-bipyridine and 6-quinoline relative to pyridine might limit these side-reactions. Therefore, the feasibility of the [2 + 1] cycloaddition reaction with 2,2′-bipyridine-based alkyne derivatives **2a-c** (prepared according to Scheme S1†) was investigated in NMR scale experiments.

Derivatives **2a-c**, 1.5 eq. $TMSCF_2Br$ and 3 mol% of the initiator TBABr were heated in toluene-d_8 adapting literature procedures for related aryl-substituted difluorocyclopropenes.[79,80] The reaction mixture was monitored by ^1H and ^{19}F NMR spectroscopy before and directly after a reaction time of 2 h (ESI, section 3†). For all three derivatives, at least one new set of signals appeared in the ^1H NMR spectra (Fig. S50, S52 and S54†) and the ^{19}F NMR spectra showed the consumption of $TMSCF_2Br$ as well as the presence of a new fluorine signal between −110 and −114 ppm (Fig. S51, S53 and S55†), which is consistent with the expected chemical shift of a difluorocyclopropene.[79,80,84,85]

The relative ratio of the unreacted alkyne and proposed difluorocyclopropene was determined by integrating the proton H_j signal (Scheme 2) due to its characteristic chemical shift and separation from other signals (Fig. S50, S52 and S54†). Derivative **2b** showed the highest product/starting material ratio (93 : 7, Table 1) and furthermore, the ^{19}F NMR spectrum showed nearly complete consumption of $TMSCF_2Br$ (Fig. S53†). In contrast, the amount of the product significantly decreased for **2a** and even more so for **2c** with a second N-heterocyclic substituent (Table 1). Thus, better conversion to the difluorocyclopropene is observed in cycloadditions with substrates containing more electron-rich R substituents, as expected.

Encouraged by the observed conversion in the NMR scale experiments, large scale syntheses were carried out in a pressure tube and difluorocyclopropenes **3a-c** were isolated in moderate to good yields following column chromatography

Table 1 Comparison of the conversions from *in situ* NMR experiments and isolated yields for the cycloaddition of substrates **2a–2c** with :CF_2

Substrate	3 : 2 ratio[a]	Isolated[b] yield (%)
2a	52 : 48	32
2b	93 : 7	50
2c	18 : 82	21

[a] Determined from NMR scale experiments (0.1 mmol of the respective alkyne substrate) and integration of the proton H_j of the difluorocyclopropene **3a-c** and alkyne **2a-c**. [b] Following column chromatography in larger scale syntheses.

(Table 1 and ESI section 2†). In addition, the X-ray crystal structure of **3a** was obtained showing the expected difluorocyclopropene structure (ESI section 2.1.2.1 and Fig. S12†). The C═C bond length (1.33 Å) and C–F bond lengths (1.38 Å) in the cyclopropene ring are similar to those in related difluorocyclopropenes.[86,87]

Although synthetic access to the desired difluorocyclopropenes was initially envisaged to be challenging, the cycloaddition strategy was tolerant of both the 2,2′-bipyridine coordination motif and a second heterocyclic 6-quinoline substituent. Furthermore, the difluorocyclopropene derivatives were stable during purification by column chromatography on silica gel. This was surprising since other difluorocyclopropenes and related difluorocyclopropanes are susceptible to hydrolysis under relatively mild conditions,[38,56,74] including on silica gel,[56,81,86,88] giving the corresponding cyclopropenones and cyclopropanones, respectively.

Indeed, attempted hydrolysis of **3a-c** to cyclopropenones **1a-c** on a small scale under a variety of mild conditions (wet $CDCl_3$, Amberlyst® 15 or silica gel at room temperature for 24 h)[38,56,74,80] revealed the stability of the difluorocyclopropenes (ESI, section 4†); while there was no hydrolysis of **3c** under these conditions (Fig. S58A–C†), derivatives **3a-b** showed partial hydrolysis using Amberlyst® 15 and silica gel (Fig. S56 and S57B, C†) and no hydrolysis in $CDCl_3$ (Fig. S56 and S57A†). In contrast, complete hydrolysis was observed using 6 M HCl since the cyclopropenone was obtained following neutralisation and extraction with $CDCl_3$ (Fig. S56 and S57D†). Despite the complete consumption of quinoline derivative **3c**, it was necessary to shorten the reaction time to 1 h to prevent the formation of a by-product (Fig. S58D and D.1†).

Further optimisation of this hydrolysis method with HCl enabled the preparative isolation of N-heterocyclic cyclopropenones in good yields (65–91%) with a reaction time of 15 min for **1a** and **1b** and 1 h for derivative **1c**. Evidence for the formation of **1a-c** was given by the distinct shift of the carbonyl carbon[39,50,89] around 150–156 ppm in the ^{13}C NMR spectra (Fig. S14, S30 and S46†), observation of the molecular ion peak in the ESI mass spectra as well as the characteristic carbonyl stretches and ring vibrations[25,28,39,90] in the ranges of 1835–1850 cm^{-1} and 1560–1625 cm^{-1} in the IR spectra (ESI sections 2.1.3, 2.2.3, 2.3.3†).

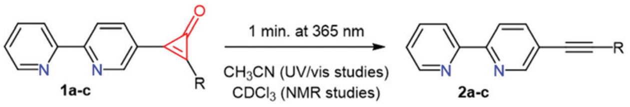
With the successful synthesis of the series of 2,2′-bipyridine-based ligands **1a-c**, the stability of this new class of cyclopropenones was investigated regarding storage and handling. No decomposition of solid samples was observed over at least a month at room temperature under ambient light. However, solutions of the cyclopropenones in $CDCl_3$ under ambient light showed evidence of decarbonylation over a period of one week (ESI section 5 and Fig. S62–64†) As a result, all cyclopropenones in solution were protected from light as a precaution.

Irradiation studies were carried out using UV/vis and NMR spectroscopy to investigate the influence of the R substituent on photodecarbonylation (Scheme 3 and ESI section 6†). Since the synthesis and study of the M-CPOnes was carried out in acetonitrile, the UV/vis spectra of ligands **1a-c** as well as reference alkyne derivatives **2a-c** were measured in acetonitrile. However, due to the limited solubility of the ligands at typical NMR concentrations in acetonitrile, the NMR studies with the ligands were performed in $CDCl_3$.

The UV/vis spectra of cyclopropenones **1a-c** show broad absorption bands and as expected based on studies of related cyclopropenones with alkyl and aryl substituents,[50] the R substituent tunes the absorption maximum from 321 nm (**1a**) to 333 nm (**1c**) and 341 nm (**1b**) (Fig. 1a). Photodecarbonylation of related cyclopropenones has been reported upon irradiation of the absorption bands around 240–325 nm and 360 nm assigned to the π–π* and n–π* transitions, respectively.[50,91–95] Irradiation of the π–π* absorption band is proposed to produce the corresponding alkyne in the excited state in contrast to the ground state following irradiation of the n–π* absorption band.[94] A wavelength of 365 nm was chosen to trigger the photodissociation in these studies for this reason and since the absorbance of the alkynes are minimal at this wavelength; in related systems, the alkyne photoproducts are reported to undergo subsequent photoreactions.[50]

Irradiation for 1 min with all cyclopropenones showed complete photodecarbonylation to the corresponding alkyne derivatives (Fig. 1b). The ^{1}H and ^{13}C NMR spectra as well as the UV/vis spectra were consistent with the reference alkyne spectra (Fig. S65–S73†). Furthermore, no by-products were observed in the NMR spectra. Complete photodecarbonylation was also observed by UV/visible spectroscopy following irradiation of **1a** for 10 s (Fig. S67†), demonstrating that the longer irradiation time of 1 min does not lead to by-product formation and suggesting efficient photodecarbonylation. The quantum yields for the photodecarbonylation of related cyclopropenones are high (Φ 0.2–1.0).[50,93]

The scope of this study is demonstration of the proof of concept of light-triggered CO release from M-CPOnes. Therefore, we chose to focus on M-CPOnes based on kinetically labile Fe^{II}, Co^{II} and Zn^{II} complexes for these initial



Scheme 3 Photodecarbonylation of cyclopropenone ligands **1a-c** to **2a-c**.

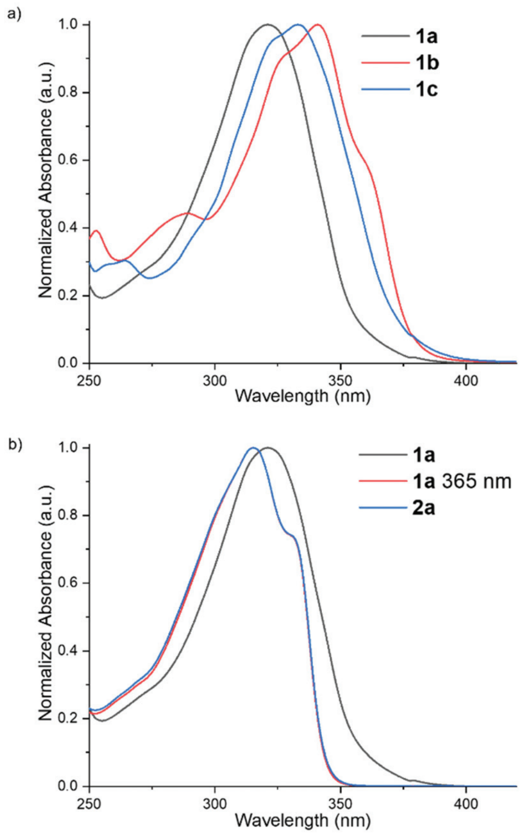


Fig. 1 Comparison of the normalized UV/vis spectra (CH_3CN, 298 K) of: (a) cyclopropenone ligands **1a–c**; (b) cyclopropenone ligand **1a** before (black) and after (red) irradiation with 365 nm for 1 min as well as the reference compound **2a** (blue).

investigations to establish the compatibility of the cyclopropenone moiety with transition metal complexes regarding stability and photodecarbonylation. M-CPOnes-**1a-c** were prepared by mixing the respective metal salt ($Fe(BF_4)_2·6H_2O$, $Zn(OTf)_2$ or $Co(NTf_2)_2$) and three equivalents of the ligand in CD_3CN and were characterised by NMR, UV/Vis, IR spectroscopy and ESI spectrometry either *in situ* or after precipitation with diethyl ether. Since these non-symmetric ligands could form a mixture of meridional (*mer*) and facial (*fac*) coordination isomers, up to four sets of NMR signals were to be expected.

In addition, the corresponding alkyne complexes M-**2a-c** (M = Fe^{II}, Zn^{II} and Co^{II}) were synthesised for comparison since they are formed upon photodecarbonylation of the M-CPOnes (Scheme 1). Although the nitrogen donor of the quinoline substituent in ligand **2c** could, in principle, also coordinate to the metal leading to ill-defined complex mixtures, the NMR spectra for complexes Fe-**2c** and Co-**2c** were consistent with metal binding to the 2,2′-bipyridine motif only when a 1 : 3 metal/ligand ratio was used (Fig. S162–166 and S168–173†).

Complexation of cyclopropenone ligands **1a** and **1b** with Zn^{II} and Fe^{II} resulted in the formation of diamagnetic complexes (Fig. S74, S75, S80, S81, S95, S96, S101 and S102†) with different ^1H and ^{13}C NMR spectra to the alkyne complexes Zn-**2a,b** and Fe-**2a,b** (Fig. S125, S126, S131, S132, S145, S146, S151, and 152†). However, complete assignment of the spectra was not possible for the Zn-CPOnes-**1a,b** due to broad linewidths and overlapping signals, although ESI mass spectra were consistent with the formation of ZnL_3 complexes (Fig. S84 and S106†). Characterisation of Fe-CPOnes-**1a,b** was also challenging given the number of overlapping signals, however, the signals for H_j were distinct and four sets were observed (Fig. S74 and S95†). This along with the observation of four sets of signals for each carbon in the ^{13}C NMR spectra suggests the formation of a mixture of *fac* and *mer* isomers (Fig. S75 and S96†). In contrast to the challenging NMR analysis with the Zn^{II} and Fe^{II} complexes due to signal overlap, the formation of paramagnetic complexes with Co^{II} resulted in greater signal dispersion due to the large paramagnetic shifts. Characterisation using our recently reported paramagnetic NMR toolbox[96] revealed four ligand environments consistent with a mixture of the *fac* and *mer* isomers (Fig. S87–S93 and S107–S112†).

Evidence for the cyclopropenone moiety being intact following complexation comes from observation of the carbonyl carbon signals in the ^{13}C NMR spectra of the diamagnetic Fe^{II} complexes at similar shifts to the free ligands as well as the distinctive carbonyl stretches and ring vibrations in the IR spectra of M-CPOne-**1a,b** (M = Fe^{II}, Zn^{II}, Co^{II}). Furthermore, ESI mass spectra confirmed the formation of M-CPOne-**1a,b** (M = Fe^{II}, Zn^{II}, Co^{II}) through the observation of the $[ML_3]^{2+}$ ion peaks as well as $[ML_3 - (CO)_n]^{2+}$ (n = 1–3) ion peaks resulting from decarbonylation under the ionisation conditions (Fig. S79, S84, S94, S100, S106 and S113†).

The photophysical properties of the cyclopropenone in M-CPOne-**1a,b** (M = Fe^{II}, Zn^{II}, Co^{II}) were similar to those of the free cyclopropenone ligand **1a** and **1b** with small bathochromic shifts of the absorption maxima in the UV/vis spectra in acetonitrile (Fig. S176, S179, S181, S184, S189 and S191†). As with the free ligands, the R substituent tunes the absorption maximum with a 30 nm difference between Fe-CPOne-**1a** and Fe-CPOne-**1b** (Fig. 2a, inset).

Irradiation experiments were carried out by UV/vis and NMR spectroscopy using 365 nm light given the similarity of the absorption maxima to those of the free ligands (Scheme 1 and Fig. 1a, 2a). Following irradiation of M-CPOne-**1a,b** (M = Fe^{II}, Zn^{II}, Co^{II}) for 1 min, UV/vis spectra consistent with the corresponding alkyne complexes M-**2a,b** were obtained, suggesting complete photodecarbonylation of M-CPOne-**1a,b** (ESI section 9†). Further studies using NMR spectroscopy supported photodecarbonylation to the corresponding alkyne complexes M-**2a,b**. However, longer irradiation times of 4 min and 20 min were required for photodecarbonylation of Co-CPOne-**1a,b** and Fe-CPOne-**1a,b**, respectively. This was attributed to the increased concentration for the NMR studies (mM *vs.* μM for NMR and UV/vis studies, respectively) and competing absorbance of the alkyne complexes at 365 nm, although competing metal-based transitions could also contribute to the longer irradiation times. There was no evidence

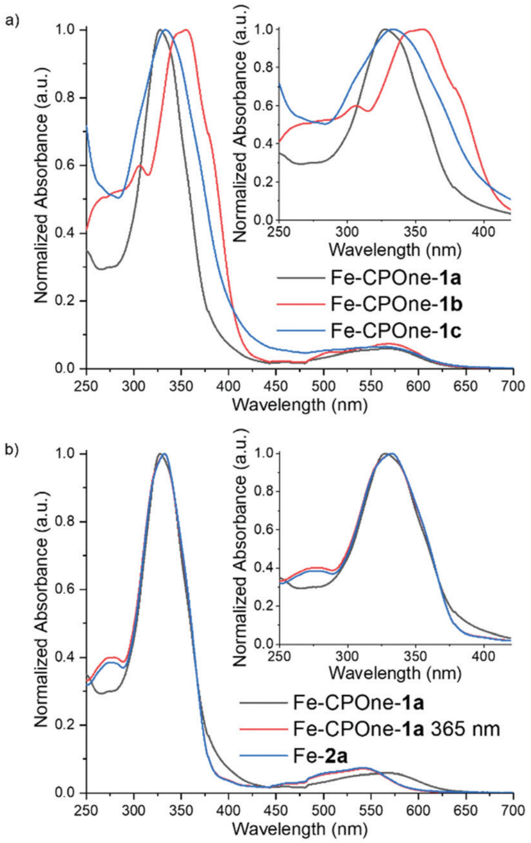


Fig. 2 Comparison of the normalized UV/vis spectra (CH_3CN, 298 K) of: (a) Fe-CPOnes-**1a-c**; (b) Fe-CPOne-**1a** before (black) and after (red) irradiation with 365 nm for 1 min as well as the reference complex Fe-**2a** (blue). The insets show an expansion of the spectra between 250 and 400 nm for comparison of the absorption maxima.

of by-product formation, for example from subsequent photoreactions of the alkyne complexes, with the longer irradiation times.

In addition to these photodecarbonylation properties, the M-CPOnes have tunable properties due to the presence of the metal. The fluorescent properties of Zn-CPOne-**1a** and its corresponding alkyne complex Zn-**2a** were also investigated. Upon excitation at 312 nm Zn-**2a** showed emission at 362 nm and a similar emission spectrum was obtained for Zn-CPOne-**1a**, although the fluorescence was weaker (Fig. S85, S86 and S177†). Similar spectra were obtained for the corresponding ligands **1a** and **2a** (Fig. S85 and S86†). We propose that Zn-CPOne-**1a** shows no/weak fluorescence and some photodecarbonylation takes place at this excitation wavelength, as observed by Popik and co-workers for related cyclopropenones.[50] Thus, the fluorescence from the photodecarbonylated products of Zn-CPOnes could be exploited as another indicator of CO release. For Fe-CPOne-**1a,b** CO release could be followed through the hypsochromic shift of the MLCT band around 570 nm upon irradiation (Fig. 2b and S181, S184†), resulting in a colour change from purple to red (Fig. S182†). Finally, photodecarbonylation of Co-CPOne-**1a,b** resulted in shifts of up to 5 ppm for the bipyridine coordination motif signals in the paramagnetic NMR spectrum (Fig. S188 and S190†).

Over the course of our studies, we found the quinoline-containing ligand **1c** showed different coordination properties to the corresponding alkyne ligand **2c** and cyclopropenone ligands **1a–1b**. Given the characterisation difficulty with Zn-CPOnes due to the broadness of the NMR spectra, we focussed on the preparation of M-CPOnes-**1c** (M = Fe^{II}, Co^{II}) using the same procedure as previously described. While ^1H NMR and mass spectra consistent with the formation of Fe-CPOne-**1c** and Co-CPOne-**1c** were observed immediately after preparation (Fig. S114, S116–S119 and S121–124†), the signals in the NMR spectra decreased in intensity over time (Fig. S115 and S120†). There was also a colour change as well as partial precipitation. We propose the observed spectral changes for Fe-CPOne-**1c** and Co-CPOne-**1c** are due to the rearrangement of kinetically formed metastable M-CPOnes-**1c** (M = Fe^{II}, Co^{II}) to a dynamic combinatorial library of multiple interconverting species. This is attributed to the presence of an additional coordination motif, the 6-quinoline, and its orientation in the bent cyclopropenone ligand given complexes M-**2c** did not rearrange.

Indeed, irradiation experiments with the proposed dynamic combinatorial library samples as well as freshly prepared M-CPOnes-**1c** (M = Fe^{II}, Co^{II}) using NMR spectroscopy showed similar NMR spectra to the respective alkyne complexes M-**1c** following irradiation at 365 nm for 4 min (M = Co^{II}) or 20 min (M = Fe^{II}). In addition, the freshly prepared M-CPOne-**1c** complexes showed spectral changes consistent with photodecarbonylation (Fig. S185, S186, S192 and S193†). This suggests that the change of the NMR spectra over time was not due to decomposition of the cyclopropenone motif but due to additional coordination events since photodecarbonylation was still possible following rearrangement to the proposed dynamic combinatorial library.

Conclusions

A family of M-CPOnes was successfully prepared as a new class of CO-releasing molecules combining the light-triggered decarbonylation of cyclopropenones with the tunability of transition metal complexes. Firstly, we demonstrated N-heterocyclic cyclopropenones based on electron-deficient 2,2′-bipyridine coordination motifs are synthetically accessible *via* a cycloaddition and subsequent hydrolysis of the difluorocyclopropenes. Furthermore, the ligands are stable to coordination with Zn^{II}, Fe^{II} and Co^{II} forming the M-CPOnes. Special handling and storage of the ligands and their corresponding M-CPOnes was not necessary, other than exclusion of ambient light for samples in solution. Upon irradiation with a suitable wavelength, photodecarbonylation of M-CPOne to the corresponding alkyne complex was observed, thus demonstrating the proof-of-concept. More detailed photophysical studies of cyclopropenone-based ligands and their corresponding M-CPOnes will be the subject of future work.

The advantage of M-CPOnes is their modularity since up to 3 CO-releasing ligands can be incorporated within one complex and their properties can be readily tuned *via* the metal ion as well as the cyclopropenone substituents. For example, the absorbance maximum of the cyclopropenones in the M-CPOnes and their corresponding ligands was modulated by the R substituent with a bathochromic shift of up to almost 30 nm for the thienyl relative to the phenyl substituent.

The presence of the metal ion confers additional properties so that the photodecarbonylation of the Zn-CPOnes could be detected by fluorescence, the Fe-CPOnes by the shift of the MLCT band and the Co-CPOnes by paramagnetic NMR spectroscopy due to the greater dispersion of the signals, particularly for the bipyridine coordination motif given its proximity to the Co^{II} centre. The ability to track photodecarbonylation by a variety of spectroscopic methods dependent on the metal ion will be beneficial for future applications of M-CPOnes.

Furthermore, M-CPOnes are compatible with incorporation of a second coordination site, 6-quinoline, and the initially formed M-CPOnes-**1c** (M = Co^{II}, Fe^{II}) were proposed to rearrange into dynamic combinatorial libraries that still undergo photodecarbonylation to the corresponding M-**2c** complexes. This opens up avenues for supramolecular M-CPOnes and will be the subject of future investigations as well as broadening the scope of the metals within M-CPOnes.

Author contributions

M. L.: conceptualisation (equal), data curation (lead), formal analysis (lead), investigation (lead), resources (lead), validation (lead), visualisation (lead), writing-original draft (lead), writing-review and editing (equal). T. N.: conceptualisation (equal), formal analysis (supporting), investigation (supporting), resources (supporting), validation (supporting), visualisation (supporting), writing-original draft (supporting), writing-review and editing (equal). C. N.: formal analysis (supporting), investigation (supporting), resources (supporting), writing-review and editing (supporting). A. J. M.: conceptualisation (lead), formal analysis (supporting), funding acquisition (lead), project administration (lead), resources (supporting), supervision (lead), visualisation (supporting), writing-original draft (supporting), writing-review and editing (equal).

Conflicts of interest

There are no conflicts to declare.

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