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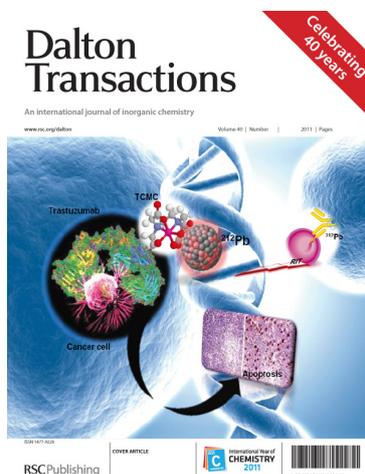


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PAPER

Binding and photodissociation of CO in iron(II) complexes for application in positron emission tomography (PET) radiolabelling†

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(R-DAB)FeI₂ complexes containing bidentate diimide ligands (R-DAB = RN=CH–CH=NR; R = ⁱPr, *c*-C₆H₁₁) have been investigated for their ability to react with carbon monoxide to form iron(II) dicarbonyl complexes, (R-DAB)FeI₂(CO)₂. Solution IR spectroscopy revealed two νCO stretches between 2000 and 2040 cm⁻¹ corresponding to a *cis*-arrangement of the carbonyl ligands around the iron. Photochemical decarbonylation was achieved by UV irradiation (365 nm), which occurred within 5 min as evidenced by solution IR spectroscopy. (*c*-C₆H₁₁-DAB)FeI₂ has been characterised by X-ray crystallography. Reactions using ¹¹C-labelled carbon monoxide were investigated and revealed that both (R-DAB)FeI₂ species were not effective as trapping complexes due to the low concentrations of [¹¹C]CO used in these experiments. A Fe(TPP)(THF)_x (TPP = tetraphenylporphyrin) complex was investigated with unlabelled CO and the monocarbonyl adduct Fe(TPP)(THF)CO was formed *in situ* as identified by IR spectroscopy (νCO = 1966 cm⁻¹) yet was stable to CO loss upon UV irradiation. Carbonylation reactions of *in situ*-generated Fe(TPP)(THF)_x using [¹¹C]CO revealed that 97% of the [¹¹C]CO stream could be trapped in one pass of the gas at room temperature and at atmospheric pressure.

Introduction

Positron emission tomography, PET, is a non-invasive technique that is used to image biological processes such as metabolic function and receptor distribution *in vivo*.¹ While most frequently used for oncology,² PET is increasingly being used by the pharmaceutical industry in drug development,^{3,4} offering the potential to visualise receptor sites and drug affinity, aiding in drug dosage calculations and determining pharmaceutical effects at a molecular level.⁵

Radiolabelling with ¹¹C is particularly appealing due to the prevalence of carbon in natural products and pharmaceuticals. ¹¹C-radiolabelling is mostly based around [¹¹C]methylation reactions using [¹¹C]methyl iodide, however, this approach is limited to labelling the periphery of the molecule (*e.g.* methylation of an amino group). In the last 15 years, [¹¹C]carbon monoxide ([¹¹C]CO) has emerged as an important labelling reagent for transition metal-mediated carbonylation reactions.⁶ In this way [¹¹C]CO can couple

two precursor moieties to form a labelled molecule containing a [¹¹C]carbonyl core. A common example is the aminocarbonylation reaction between an amine and an aryl halide with [¹¹C]CO to form a [¹¹C-*carbonyl*]amide. Despite its great potential for tracer synthesis, the widespread use of [¹¹C]CO in PET has been hindered by its poor solubility, leading to low radiochemical yields under standard conditions. This has led researchers to examine methods of increasing its reactivity through the use of high pressure autoclave reactors,^{7,8} or by improving solubility at low pressures through chemical complexation in solution for subsequent release using heat⁹ or ligand addition.¹⁰

In order to extend this solution chemistry, we decided to examine the potential of iron complexes to trap CO in solution for subsequent mild (low temperature, competing ligand-free) CO release *via* UV irradiation. Iron(II) complexes, were particularly appealing due to the high abundance, low cost and biological and environmental compatibility of iron.¹¹ Here, we report the reactivity of iron(II) complexes containing bidentate, 1,4-diazabuta-1,3-diene (R-DAB), and tetradentate, tetraphenylporphyrin (TPP), N-donor ligands towards [¹²C]CO and [¹¹C]CO and examine their potential for rapid decarbonylation *via* UV photolysis.

Discussion

1,4-Diazabuta-1,3-dienes (R-DAB) ligands, form a useful class of bidentate α-diimine ligands which are readily coordinated to iron(II) halides to form four coordinate complexes.^{12,13} The ligands can be readily prepared in high yield by condensation

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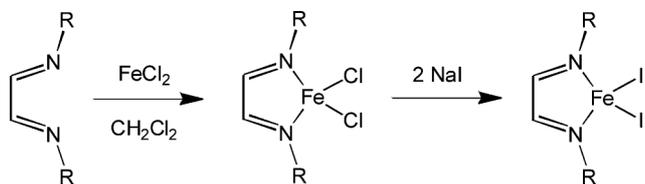
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† Electronic supplementary information (ESI) available. CCDC reference number 725949. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt01614d

of glyoxal with two equivalents of the appropriate amine.¹⁴ In 1999 Spek *et al.*¹⁵ reported that (*i*-Pr-DAB)FeI₂ could be reversibly formed by thermal or photochemical decarbonylation of (*i*-Pr-DAB)FeI₂(CO)₂ which was itself formed by oxidative addition of iodine to the stable zero-valent iron complex (*i*-Pr-DAB)Fe(CO)₃.¹⁵ We sought to explore this system for its potential use in [¹²C]CO trapping experiments in the radiochemical laboratory.

Our initial studies found that the corresponding chloro-substituted complexes, (R-DAB)FeCl₂, were unreactive towards CO. This difference in reactivity may result from small variations in electron density. We suggest that the chloro complex has, through greater electronegativity, insufficient electron density available to stabilise the Fe–CO bond by back-bonding, whereas iodo ligands are generally better π -donors thus resulting in a more electron-rich iron centre. As such, we sought a new synthetic approach to the iodo-substituted species (R-DAB)FeI₂ that did not involve manipulation of the tricarbonyl species, for potential application in rapid [¹²C]CO trapping. The direct reaction of FeI₂ with the R-DAB ligands was found to produce undesired side reactions with no traces of the desired product. However, it was found that the iodo complexes could be synthesised *in situ* by ligand exchange of the corresponding stable (R-DAB)FeCl₂ complex using sodium iodide (Scheme 1).



Scheme 1 Synthesis of (R-DAB)iron(II) dihalide complexes (R = *i*-Pr, *c*-C₆H₁₁).

Both cyclohexyl and isopropyl R groups were chosen as their moderate steric bulk was hoped to provide a degree of stabilisation to the coordinated iron centre whilst not blocking the approach of the CO molecules. The intermediate (R-DAB)FeCl₂ complexes were isolated as purple solids in moderate yield by 1 : 1 reaction of the corresponding R-DAB ligand with anhydrous iron(II) chloride in dichloromethane. As tetrahedral 14e⁻ complexes, their resultant paramagnetism caused significant line broadening in their ¹H NMR spectra. Mass spectrometry was used to confirm the presence of the parent complexes and elemental analysis provided an excellent match to the calculated values for both (*i*-Pr-DAB)FeCl₂ and (*c*-C₆H₁₁-DAB)FeCl₂. The corresponding iodo-substituted complexes (*i*-Pr-DAB)FeI₂ and (*c*-C₆H₁₁-DAB)FeI₂ were formed by addition of two equivalents of sodium iodide to the chloro-complexes and stirring overnight, in each case the purple solution becoming dark green. Filtration followed by removal of the solvent gave the iodo-species as dark green solids. It was not possible to obtain an analytically pure sample of (*i*-Pr-DAB)FeI₂, although this compound has been isolated previously and structurally characterised.¹⁵

Crystals of the cyclohexyl-substituted species, (*c*-C₆H₁₁-DAB)FeI₂, were grown by slow diffusion of hexane into a dichloromethane solution and analysed by X-ray crystallography (Fig. 1). The structure reveals that the iron centre is coordinated tetrahedrally to two iodo ligands and the two N-donors of the DAB ligand. As was seen for the previously reported structure of

Table 1 Selected bond lengths (Å) and angles (°) for (*c*-C₆H₁₁-DAB)FeI₂

Fe–I	2.5662(7)	Fe–N(1)	2.102(5)
Fe–I'	2.5662(7)	Fe–N(1')	2.102(5)
N(1)–C(1)	1.263(9)	C(1)–C(1')	1.473(12)
I–Fe–N(1)	115.31(13)	I–Fe–I'	117.05(5)
I–Fe–N(1')	112.28(13)	N(1)–Fe–I'	112.28(13)
N(1)–Fe–N(1')	78.9(3)	I'–Fe–N(1')	115.31(13)

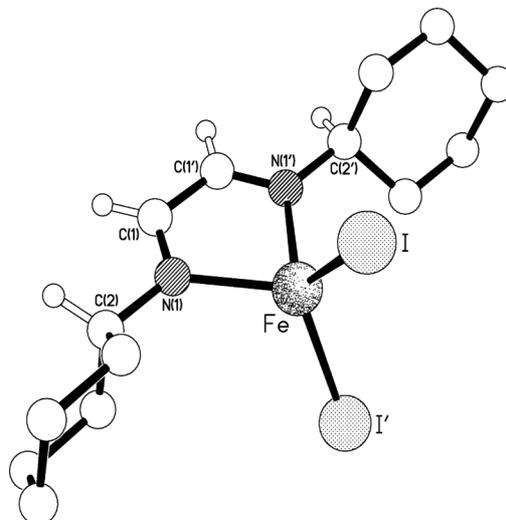


Fig. 1 The molecular structure of (*c*-C₆H₁₁-DAB)FeI₂ (atoms flagged with a prime (') character are at equivalent position: 3/2 – x, y, 1 – z).

(*i*-Pr-DAB)FeI₂,¹⁵ (*c*-C₆H₁₁-DAB)FeI₂ displays crystallographic C₂ symmetry about an axis that passes through the iron centre and bisects the C(1)–C(1') bond. Bond distances and angles are shown in Table 1.

Trap and release of [¹²C]carbon monoxide

Carbonylation and photolysis reactions on solutions of (R-DAB)FeI₂ (generated in dichloromethane solution *in situ* from (R-DAB)FeCl₂) were performed in a Pyrex immersion well apparatus using a Philips HPK 125, 400 W high-pressure mercury lamp irradiating at 365 nm (see Fig. 2). During carbonylation of the complex, CO was bubbled through the solution for 60 min. Solution IR spectra were recorded at regular intervals using aliquots of reaction solution which were removed from the apparatus by syringe.

During the carbonylation of the (R-DAB)FeI₂ complexes (R = *c*-C₆H₁₁, *i*-Pr), in each case the solution changed from dark green to dark pink in colour (Fig. 2, RHS) and IR spectroscopy (Fig. 3) indicated the coordination of CO to the complex *via* the appearance of carbonyl peaks at around 2000 and 2040 cm⁻¹. These two peaks suggest that two carbonyl groups are bound to each iron centre in a *cis*-arrangement, thus forming hexacoordinate complexes of the formula (R-DAB)FeI₂(CO)₂. Previously reported¹⁵ data for (*i*-Pr-DAB)FeI₂(CO)₂ shows two ν CO absorptions at 2400 and 2000 cm⁻¹, in agreement with our findings.

Following the formation of both (R-DAB)FeI₂(CO)₂ complexes, photodissociation reactions were investigated by irradiating each solution with UV light (365 nm) for 5 min while a continuous stream of nitrogen gas was bubbled through the solution. This

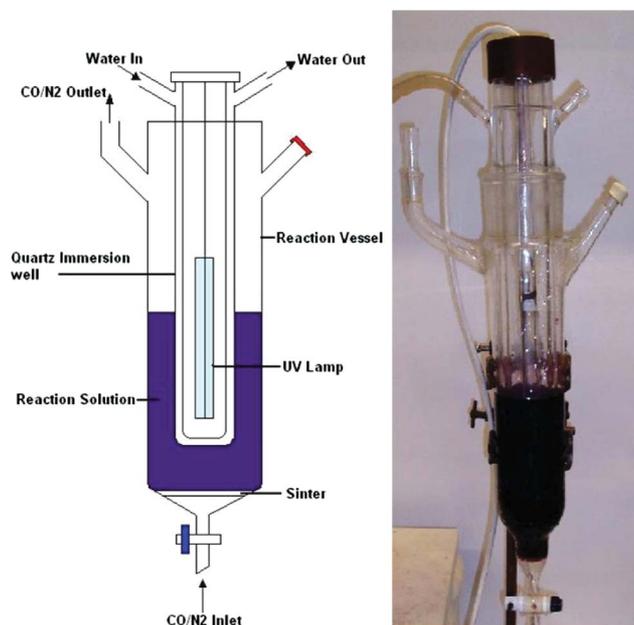
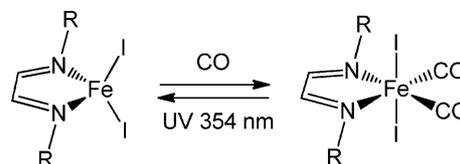


Fig. 2 Schematic and photograph of the UV apparatus used in the carbonylation of $(\mathbf{R-DAB})\text{FeI}_2$.

caused the dark pink solutions to revert back to their original dark green colour, indicating reformation of the carbonyl-free species. UV-vis spectra were not collected as the IR data was more informative, but similar observations were noted to the analogous compounds reported in reference 15. Solution IR

spectra performed on an aliquot of solution removed from the vessel showed complete removal of the carbonyl stretches for both species. In order to examine the potential reversibility of this process, the irradiation was stopped and CO was once more bubbled through the solutions for 30 min. As before, the conversion from dark green solution to dark pink solution was observed along with the appearance of strong bands in the IR spectra at 2040 and 2000 cm^{-1} (Fig. 3). This indicates that the process is indeed reversible as shown in Scheme 2. In addition to the CO-trap/UV-release reactions, a pair of control reactions were performed to observe the effect of bubbling N_2 gas through the newly formed $(\mathbf{R-DAB})\text{FeI}_2(\text{CO})_2$ solutions in the absence of UV light. For both species, it was found that after 12 h of N_2 bubbling there was no significant reduction in the intensity of the carbonyl bands in the IR spectra.



Scheme 2 Carbonylation and photolysis reaction of $(\mathbf{R-DAB})\text{FeI}_2$.

In addition to the study of the CO binding to $(\mathbf{R-DAB})\text{FeI}_2$ complexes, a synthetic heme analogue consisting of tetraphenylporphyrin (TPP) coordinated to iron(II) was similarly investigated. Since the Nobel prize-winning determination of the structures of hemoglobin and myoglobin in the 1960s by Perutz and Kendrew, considerable work has been directed towards the synthesis of

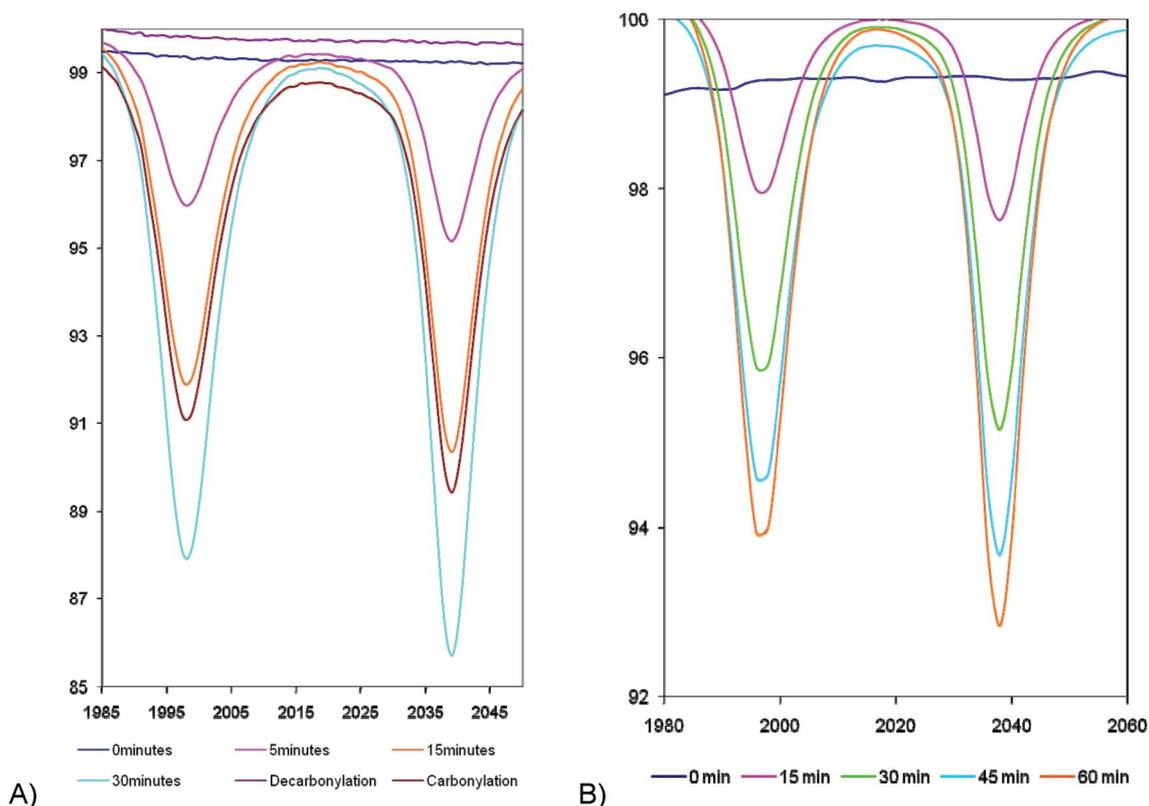


Fig. 3 IR spectra showing A) the trap and release of $[^{12}\text{C}]\text{CO}$ to $(\mathbf{Pr-DAB})\text{FeI}_2$ and B) the trapping of $[^{12}\text{C}]\text{CO}$ by $(\mathbf{c-C}_6\text{H}_{11}\text{-DAB})\text{FeI}_2$.

synthetic heme analogues as models to study dioxygen and carbon monoxide binding to heme proteins.¹⁶ The well-established binding of CO to the iron centre in heme units provided an ideal system for application in the rapid binding of [¹¹C]CO for potential radiolabelling experiments. Furthermore, photodissociation of CO from iron(II) porphyrins is well known, with flash photolysis having been used to measure the kinetics of O₂ and CO binding.¹⁶

The tetraphenylporphyrin iron(II) complex, (TPP)Fe(THF)_x was synthesised *in situ* by the reduction of tetraphenylporphyrin iron(III) chloride in THF giving the characteristic deep red solution. CO was bubbled through this solution following the same procedure as for the (R-DAB)FeI₂ complexes and solution IR spectra were recorded periodically. Formation of the carbonyl adduct was confirmed by solution IR spectroscopy which showed a CO stretch appearing at 1966 cm⁻¹ within 1 min of CO bubbling, while prolonged bubbling did not lead to a significant increase in the intensity of this band (Fig. 4). This CO stretch falls within the typical region for a six coordinate, low-spin Fe(II)(porphyrin) complex,¹⁷ and is in reasonable agreement with that previously reported for (TPP)FeCO (1973 cm⁻¹)¹⁸ and excellent agreement with the low temperature IR spectrum of (TPP)Fe(THF)CO reported by Kurtikyan *et al.*¹⁹ Formation of the dicarbonyl species would be expected to lead to an increase in νCO to around 2040 cm⁻¹ as a result of competitive π-back bonding between the *trans* CO groups and no such absorption was observed during our experiments. These observations led us to conclude that the monocarbonyl adduct (TPP)FeCO(THF) has been formed in our experiments.

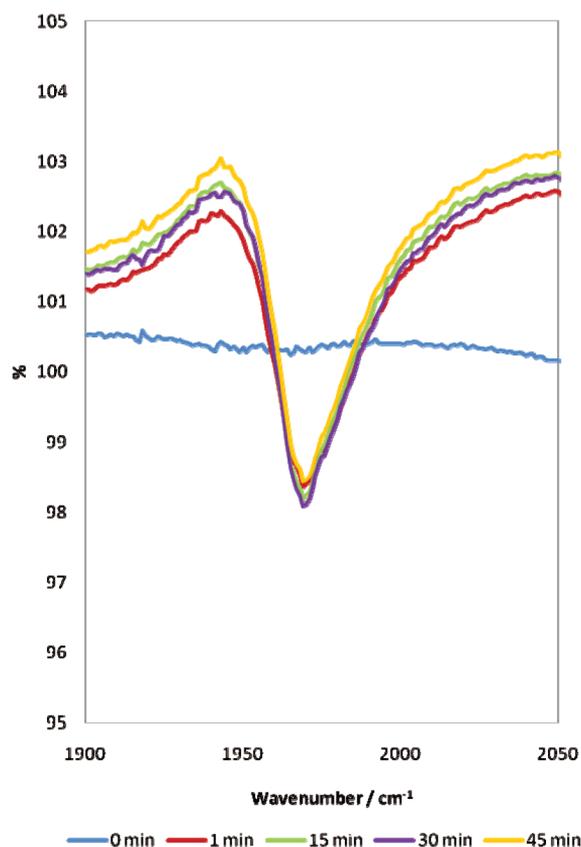


Fig. 4 IR spectra of (TPP)Fe(THF)_x in THF solution upon reaction with CO.

As for the (R-DAB)FeI₂ complexes, photodissociation experiments were attempted by irradiating the solution with UV light at 365 nm. This did not lead to any noticeable reduction in the intensity of the CO stretch in the solution IR spectrum despite prolonged (1 h) irradiation. It is thought that this phenomenon might be caused by rapid recombination of CO to the complex despite the presence of the purging nitrogen gas stream.¹⁷ Alternatively, it may indicate the need for an irradiating light source of a different wavelength and this will be the subject of future studies.

[¹¹C]CO trapping experiments

Having observed rapid CO uptake by both the bidentate and tetradentate iron(II) complexes, using unlabelled CO, the uptake of ¹¹C-labelled carbon monoxide, [¹¹C]CO was investigated in the radiochemical laboratory. The conditions for radiolabelling experiments vary significantly from those used with unlabelled CO due to the small amounts of ¹¹C generated by the cyclotron. In a typical experiment it is estimated that nanomolar quantities of [¹¹C]CO are produced in the radiochemical laboratory, with the gas being delivered to the reaction solution diluted in a helium carrier gas stream. In our experiments the gas stream was delivered *via* a needle to a glass sample vial containing the iron(II) complex in THF (1 mL of a 11 mM solution). For each experiment the [¹¹C]CO/He gas stream was bubbled through the solution at a flow rate of 20 mL min⁻¹ and the waste gases, having passed through the vial, were collected in a gas bag situated in a dose calibrator providing real-time radioactivity measurements of the untrapped gases. Following delivery of the [¹¹C]CO to the vial, the radioactivity of the sample vial was measured. From this the trapping efficiency was calculated as the fraction of the radioactivity of the sample vial over the total amount of [¹¹C]CO delivered to the system (vial radioactivity + waste gas radioactivity). The trapping efficiencies of (⁶Pr-DAB)FeI₂, (*c*-C₆H₁₁-DAB)FeI₂ and (TPP)Fe(THF)_x from these experiments are shown in Table 2.

As can be seen, the trapping efficiencies of the (R-DAB)FeI₂ complexes were very low compared with (TPP)Fe(THF)_x. The (R-DAB)FeI₂ trapping efficiencies are comparable to that found in the solvent alone, indicating that the iron(II) complexes do not contribute significantly to CO binding. This is in contrast to the rapid CO binding observed in the corresponding reactions using unlabelled CO, and is attributed to the reversal in stoichiometries that occurs when switching to the radiochemical laboratory. In the latter, there is an excess of iron(II) complex relative to the [¹¹C]CO meaning that formation of the dicarbonyl species (R-DAB)FeI₂ is statistically highly unlikely. Since the monocarbonyl species has not been isolated or observed in our experiments, it is assumed that this species is energetically unstable and hence does

Table 2 [¹¹C]CO Trapping efficiencies of Fe(II) solutions

	Trapping efficiency / % ^a
(⁶ Pr-DAB)FeI ₂	6.1 ± 0.2
(<i>c</i> -C ₆ H ₁₁ -DAB)FeI ₂	12.5 ± 0.7
(TPP)Fe(THF) _x	96.9 ± 0.1

^a Trapping efficiency calculated as a fraction of [¹¹C]CO trapped in vial *versus* total amount of [¹¹C]CO delivered to the vial. Average of two runs.

not form in these experiments. $(\text{TPP})\text{Fe}(\text{THF})_x$, however, is able to trap the $[^{11}\text{C}]\text{CO}$ almost quantitatively (97%). This compares favourably with the existing solution-based trapping media used in PET radiolabelling experiments. $\text{Cu}(\text{Tp}^*)$ complexes of the same concentration (11 mM) have shown a 96% trapping efficiency,¹⁰ while $\text{BH}_3\cdot\text{THF}$ been reported to trap >90% of the $[^{11}\text{C}]\text{CO}$.⁹

Conclusions

$(\text{Pr-DAB})\text{FeI}_2$ and $(c\text{-C}_6\text{H}_{11}\text{-DAB})\text{FeI}_2$ complexes have been found to rapidly combine with CO to form dicarbonyl $(\text{R-DAB})\text{FeI}_2(\text{CO})_2$ species, with UV triggered decarbonylation being observed within 5 min as observed by IR spectroscopy. $(\text{TPP})\text{Fe}(\text{THF})_x$ also showed rapid CO binding yet decarbonylation could not be triggered under our experimental conditions. Despite their potential for rapid trapping and release of unlabelled CO, the $(\text{R-DAB})\text{FeI}_2$ complexes were not successful at trapping $[^{11}\text{C}]\text{CO}$ due to the small quantities of this gas being produced in PET experiments. $(\text{TPP})\text{Fe}(\text{THF})_x$ however, provided an excellent system for rapid $[^{11}\text{C}]\text{CO}$ capture and we are currently examining methods of releasing this gas for use in radiolabelling experiments for the synthesis of PET tracer molecules and biologically-relevant compounds.

Experimental

All reagents were used as received from commercial suppliers. HPLC quality solvents were dried with alumina beads and sparged with nitrogen. All glassware was pre-dried in an oven at 120 °C overnight prior to use. All manipulations were performed under a nitrogen atmosphere using standard Schlenk line techniques. All analytical data were recorded in the Department of Chemistry, Imperial College London, unless otherwise stated. ^1H and ^{13}C NMR spectra were obtained at room temperature using Bruker 400 MHz spectrometers. Chemical shifts were recorded relative to internal solvent standards. IR spectra were obtained using a Perkin Elmer FT-IR Spectrometer Paragon 1000. Photolyses were carried out in a Pyrex immersion well apparatus using a Philips HPK 125 high-pressure mercury lamp. Mass spectra were recorded using EI, FAB or electrospray methods. Diffraction data were collected on an Oxford Diffraction Xcalibur 3 diffractometer using $\text{Mo-K}\alpha$ radiation. Microanalyses were carried out by Mr. Stephen Boyer at the London Metropolitan University. $[^{11}\text{C}]\text{Carbon dioxide}$ was produced using a Siemens Eclipse HP cyclotron by proton bombardment of a target containing nitrogen and 1% oxygen. $[^{11}\text{C}]\text{CO}$ was produced using an Eckert and Zeigler modular lab system using a molybdenum reductant (850 °C) and delivered to the trapping solution in a helium stream at a flow rate of 20 mL min^{-1} . The **R-DAB** ligands were synthesised *via* modification of a procedure reported by Kleigman and Barnes.¹⁴ Complexation of **R-DAB** ligands with FeCl_2 was performed according to the procedure by Dieck and Dietrichs.²⁰

Synthesis of $(\text{Pr-DAB})\text{FeCl}_2$ [compound previously reported by Kleigman and Barnes¹⁴]

Isopropylamine (4.29 ml, 50 mmol) was cooled to 0 °C and glyoxal (40% wt in water) (2.86 ml, 25 mmol) added dropwise to produce an off-white solution. This was stirred for 24 h at room temperature producing white crystals. The solid was heated to dissolve the

crystals leading to a brown solution with two layers. The top layer was separated and left to cool forming tan coloured crystals (2.15 g, 15 mmol, 62%). Mpt.: 53–56 °C. IR (nujol): $\nu(\text{C}=\text{N})$ 1632 cm^{-1} . ^1H NMR (CDCl_3) δ = 7.94 (s, 2H, $-\text{CH}=\text{N}$), 3.53 [septet, 2H, $-\text{CH}(\text{Me})_2$, $^3J_{\text{HH}}$ 6.3 Hz], 1.23 [d, 12H, $-\text{CH}(\text{CH}_3)_2$, $^3J_{\text{HH}}$ = 6.3 Hz]. ^{13}C NMR (300 K, 400 MHz, CDCl_3): δ = 159.7 [s, $-\text{CH}=\text{N}$], 61.2 [s, $-\text{CH}(\text{CH}_3)_2$], 23.7 [s, $-\text{CH}(\text{CH}_3)_2$]. UV (THF): λ_{max} = 222, 277 nm. MS (FAB): m/z = 99 (60%, $[\text{C}_5\text{H}_9\text{N}_2]^+$) 140 (27%, $[\text{C}_8\text{H}_{16}\text{N}_2]^+$).

Synthesis of $c\text{-C}_6\text{H}_{11}\text{-DAB}$ [compound previously reported by Kliegman and Barnes¹⁴]

Cyclohexylamine (0.92 ml, 8 mmol) in methanol (10 ml) was cooled to 0 °C. Glyoxal (40 wt% in water) (0.27 ml, 4 mmol) was added to the solution and stirred for 15 min. The solution was warmed to room temperature and left to stir for 2 h forming a white crystalline solid which was collected by filtration and recrystallised from methanol–water (0.27 g, 1.2 mmol, 31%). Mpt.: 151–157 °C. IR (nujol): $\nu(\text{C}=\text{N})$ 1622 cm^{-1} . ^1H NMR (CDCl_3): δ = 1–2 [m, 20H, cyclohexyl-H], 3.19 [m, 2H, $\text{HC}-\text{N}$], 7.96 [s, 2H, $\text{N}=\text{CH}$]. ^{13}C NMR: δ = 24.6 [$-\text{CH}_2-$], 25.5 [$-\text{CH}_2$], 34.0 [$-\text{CH}_2\text{CH}$], 69.5 [$-\text{CH}-\text{N}$], 160.1 [$\text{N}=\text{CH}$]. UV (diethyl ether): 232, 280 nm. MS (FAB): m/z = 55 (100%, $[\text{C}_2\text{H}_2\text{N}_2]^+$), 82 (95%, $[\text{C}_6\text{H}_{10}]^+$), 177 (80%, $[\text{C}_{11}\text{H}_{17}\text{N}_2]^+$) 220 (7%, $[\text{C}_{14}\text{H}_{24}\text{N}_2]^+$).

Synthesis of $(\text{Pr-DAB})\text{FeCl}_2$

(Pr-DAB) (0.70 g, 5 mmol) and iron(II) dichloride (0.63 g, 5 mmol) were dissolved in dry diethyl ether (50 ml) and stirred for 30 min. The sample was concentrated to dryness under vacuum and the resultant solid washed with hexane (2×20 ml). Dichloromethane (50 ml) was added and the solution was filtered and the filtrate concentrated to dryness under vacuum to give a dark purple solid (0.43 g, 1.9 mmol, 32%). ^1H NMR (CDCl_3): δ = 7.29 [s(br), $-\text{HC}=\text{N}$], 3.78 [s(br), $\text{N}-\text{CH}(\text{CH}_3)_2$], 1.89 [s(br), $\text{N}-\text{CH}(\text{CH}_3)_2$]. MS (FAB): m/z = 231 (10%, $[\text{C}_8\text{H}_{16}\text{N}_2\text{FeCl}]^+$). Anal. (%) calc. (found) for $\text{C}_8\text{H}_{16}\text{Cl}_2\text{FeN}_2$: C, 36.0 (36.1); H, 6.0 (6.0); N, 10.5 (10.4).

Synthesis of $(c\text{-C}_6\text{H}_{11}\text{-DAB})\text{FeCl}_2$

$c\text{-C}_6\text{H}_{11}\text{-DAB}$ (1.10 g, 5 mmol) and iron(II) dichloride (0.64 g, 5 mmol) were dissolved in dry dichloromethane (50 ml) and stirred overnight. Dichloromethane was removed under vacuum and the precipitate washed with hexane (2×20 ml). The precipitate was dissolved in dichloromethane, the solution was filtered and the solvent evaporated to dryness to leave a purple solid (0.53 g, 1.5 mmol, 30%). ^1H NMR (CDCl_3): δ = 5.36 [s(br), $-\text{HC}=\text{N}$], 3.80 (s(br), cyclohexyl- CH_2), 2.45 [s(br), $-\text{N}-\text{CH}$], 1.90 [s(br), cyclohexyl- CH_2CH_2]. Mass spec (FAB): m/z = 311 (65%, $[\text{C}_{14}\text{H}_{24}\text{N}_2\text{FeCl}]^+$). Anal. (%) calc. (found) for $\text{C}_{14}\text{H}_{24}\text{Cl}_2\text{FeN}_2$: C, 48.4 (48.4); H, 7.0 (6.8); N, 8.1 (8.0).

Synthesis of $(\text{Pr-DAB})\text{FeI}_2$ [compound previously reported by Breuer *et al.*¹⁵]

$(\text{Pr-DAB})\text{FeCl}_2$ (0.10 g, 0.37 mmol) was dissolved in dichloromethane (50 ml) and sodium iodide (0.11 g, 0.74 mmol) added. The dark purple solution was stirred overnight turning dark green and on removal of the solvent it formed a sticky black

solid. $^1\text{H NMR}$ (CDCl_3): 7.73 [s, $\text{N}=\text{CH}$], 4.26 [s, $-\text{CH}(\text{CH}_3)_2$], 1.35 [s, $-\text{CH}(\text{CH}_3)_2$].

Synthesis of (*c*- C_6H_{11} -DAB) FeI_2

(*c*- C_6H_{11} -DAB) FeCl_2 (0.10 g, 0.3 mmol) was dissolved in dichloromethane (50 ml) and sodium iodide (0.09 g, 0.6 mmol) added. The solution was stirred overnight, filtered and the solvent removed under vacuum to give a dark green precipitate. Single crystals suitable for X-ray analysis were grown by slow diffusion of hexane into a dichloromethane solution. Anal. (%) calc. (found) for $\text{C}_{14}\text{H}_{24}\text{FeI}_2\text{N}_2$: C, 31.7 (31.9); H, 4.6 (4.5); N, 5.3 (5.2). Mass spec (FAB): $m/z = 403$ (60%, $[\text{C}_{14}\text{H}_{24}\text{N}_2\text{Fe}]^+$).

Trap and release of carbon monoxide from (R-DAB) FeI_2 [based on method reported by Breuer *et al.*¹⁵]

(R-DAB) FeCl_2 (0.10 g, [R = ^iPr 0.38 mmol; *c*- C_6H_{11} : 0.29 mmol]) and sodium iodide (0.09 g, 0.60 mmol) was dissolved in dichloromethane (50 mL) and stirred overnight forming a dark green solution. The solution was filtered and transferred into the UV apparatus and dichloromethane (100 mL) added. An excess of CO was then bubbled through the solution for 60 min causing the solution to become dark pink in colour. Solution IR spectra were recorded at regular time intervals using an aliquot of solution removed from the vessel. (^iPr -DAB) $\text{FeI}_2(\text{CO})_2$: IR (DCM): $\nu\text{CO} = 1998, 2039 \text{ cm}^{-1}$. (*c*- C_6H_{11} -DAB) $\text{FeI}_2(\text{CO})_2$: IR (DCM): $\nu\text{CO} = 1997, 2038 \text{ cm}^{-1}$. Following the carbonylation reactions, the CO stream was stopped and replaced by a nitrogen stream and the solution irradiated by UV light at 365 nm for 5 min. Solution IR spectra were recorded for each complex using an aliquot of solution removed from the vessel and in each case the absence of νCO indicated that the CO had dissociated.

Synthesis of (TPP) $\text{FeCO}(\text{THF})$ [variation of a procedure by Wayland *et al.*¹⁸]

Tetraphenylporphyrin iron(III) chloride (50 mg, 0.07 mmol) was dissolved in tetrahydrofuran (50 ml) and sodium borohydride (38 mg, 1 mmol) added in excess. The solution was stirred for 2 h forming a dark red solution. CO was then bubbled through the solution for 60 min forming a dark yellow solution. IR (THF): $\nu\text{CO} = 1966 \text{ cm}^{-1}$. Following the carbonylation reactions, the CO stream was stopped and replaced by a nitrogen stream and the solution irradiated by UV light at 365 nm for 60 min. Solution IR spectra were recorded at intervals using an aliquot of solution removed from the vessel and in each case showed νCO to remain intact.

Attempted synthesis of (^iPr -DAB) FeI_2 (^{11}C)CO₂ and (*c*- C_6H_{11} -DAB) FeI_2 (^{11}C)CO₂

(R-DAB) FeI_2 [R = ^iPr 2.94 mg; *c*- C_6H_{11} 3.81 mg] (11 μmol , [Fe] = 11 mM) was placed in a 5 ml glass vial and flushed with nitrogen. Dry THF (1 ml) and sodium iodide was added to form the iodide complex in solution. A ^{11}C CO/He gas stream was delivered to the vial, with the waste gases being collected in a bag situated inside a dose calibrator. Once the radioactivity of the vial had reached a maximum as judged by a radioactivity sensor placed adjacent to the vial (pin diode detector), the vial was sealed and its radioactivity measured in a dose calibrator.

Synthesis of (TPP) Fe^{11}C CO(THF)

Tetraphenylporphyrin iron(III) chloride (38.3 mg, 54.5 μmol) was dissolved in THF (5 ml) and sodium borohydride (3.8 mg, 0.1 mmol) was added to form the reduced complex (TPP) $\text{Fe}(\text{THF})_x$ in solution. A 5 ml glass vial was flushed with nitrogen and (TPP) $\text{Fe}(\text{THF})_x$ (1 ml, 11 μmol of Fe, [Fe] = 11 mM) added. A ^{11}C CO/He gas stream was delivered to the vial, with the waste gases being collected in a bag situated inside a dose calibrator. Once the radioactivity of the vial had reached a maximum as judged by a radioactivity sensor placed adjacent to the vial (pin diode detector), the vial was sealed and its radioactivity measured in a dose calibrator.

Crystal data for (*c*- C_6H_{11} -DAB) FeI_2 : $\text{C}_{14}\text{H}_{24}\text{FeI}_2\text{N}_2$, $M = 530.00$, monoclinic, $I2/a$ (no. 15), $a = 13.0697(4)$, $b = 7.0217(4)$, $c = 20.4319(8)$ Å, $\beta = 98.020(4)^\circ$, $V = 1856.73(11)$ Å³, $Z = 4$ (C_2 symmetry), $D_c = 1.896 \text{ g cm}^{-3}$, $\mu(\text{Cu-K}\alpha) = 32.535 \text{ mm}^{-1}$, $T = 173 \text{ K}$, brown blocks, Oxford Diffraction Xcalibur PX Ultra diffractometer; 1789 independent measured reflections ($R_{\text{int}} = 0.0480$), F^2 refinement, $R_1(\text{obs}) = 0.062$, $wR_2(\text{all}) = 0.158$, 1604 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$], $2\theta_{\text{max}} = 143^\circ$], 88 parameters. CCDC 725949.

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