

Supplementary Information

Controlled CO release using photochemical, thermal and electrochemical approaches from the Amino Carbene complex, [(CO)₅CrC(NC₄H₈)CH₃]

Suzanne McMahon^a, Jonathan Rochford^b, Yvonne Halpin,^a Jennifer C. Manton^a, Emma C. Harvey^a, Gregory M. Greetham^c, Ian P. Clark^c, A. Denise Rooney^d, Conor Long^a and Mary T. Pryce,^{a*}

^a School of Chemical Sciences, Dublin City University, Dublin 9, Ireland,

^b Department of Chemistry, University of Massachusetts Boston, 100 Morrissey Boulevard, Boston, Massachusetts 02125, United States

^c Central Laser Facility, Science & Technology Facilities Council, Rutherford Appleton Laboratory, Harwell Science and Innovation Campus, Didcot, OX11 0QX, United Kingdom

^d Chemistry Department, National University of Ireland Maynooth, Co. Kildare.

* To whom correspondence should be addressed:

Fax: +353 1 7005503; Tel: +353 1 7008005; E-mail: mary.pryce@dcu.ie

1. General Experimental Considerations.....	S3
2. Synthesis and Structural Characterisation of $[(\text{CO})_5\text{CrC}(\text{NC}_4\text{H}_8)\text{Me}]$.....	S4
3. CO Release tests using a myoglobin assay.....	S7
4. Cyclic Voltammetry and Gas Chromatography.....	S8
5. Picosecond Time Resolved Infrared Spectroscopy.....	S10
6. Quantum Chemical Calculations.....	S11

1. General Experimental Considerations

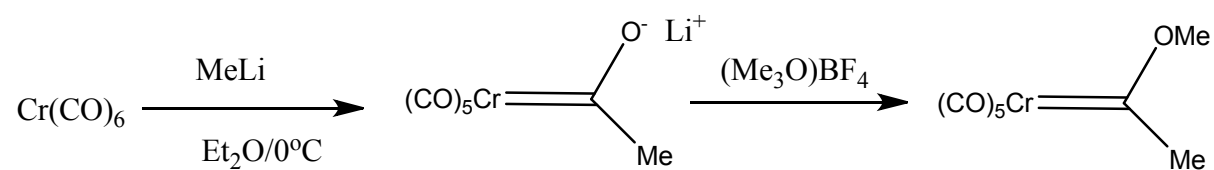
Operations were carried out in an inert atmosphere of nitrogen gas using standard Schlenk techniques. Purification was carried out by column chromatography using silica gel. Reagents and solvents were obtained from Sigma Aldrich and were used without any further purification. Anhydrous MgSO_4 was used to dry organic extracts. Volatiles were removed under reduced pressure.

IR spectra were recorded on a Perkin-Elmer 2000 FTIR spectrophotometer (2 cm^{-1} resolution) in a 0.1 mm sodium chloride liquid cell using spectroscopic grade *n* - heptane. All ^1H NMR spectra were recorded using a Bruker AC 400 spectrophotometer in CDCl_3 and were calibrated according to the deuterated solvent peak. All UV spectra were measured using an Agilent 8453 UV-Vis spectrophotometer in a 1 cm quartz cell using spectrophotometric grade *n* - heptane.

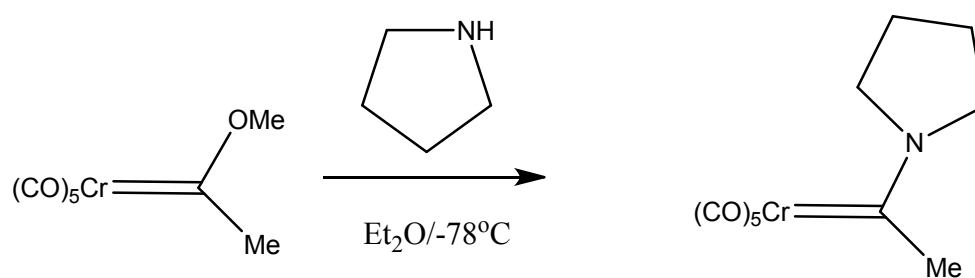
2. Synthesis and Structural Characterisation of $[(\text{CO})_5\text{CrC}(\text{NC}_4\text{H}_8)\text{Me}]$

Synthesis of $[(\text{CO})_5\text{CrC}(\text{NC}_4\text{H}_8)\text{Me}]$

The synthesis of $[(\text{CO})_5\text{CrC}(\text{NC}_4\text{H}_8)\text{Me}]$ was carried out according to previously reported procedures.^{1,2}



Scheme S1 Synthesis of $[(\text{CO})_5\text{CrC}(\text{OMe})\text{Me}]$



Scheme S2 Synthesis of $[(\text{CO})_5\text{CrC}(\text{NC}_4\text{H}_8)\text{Me}]$

Structural Characterisation of $[(\text{CO})_5\text{CrC}(\text{NC}_4\text{H}_8)\text{Me}]$

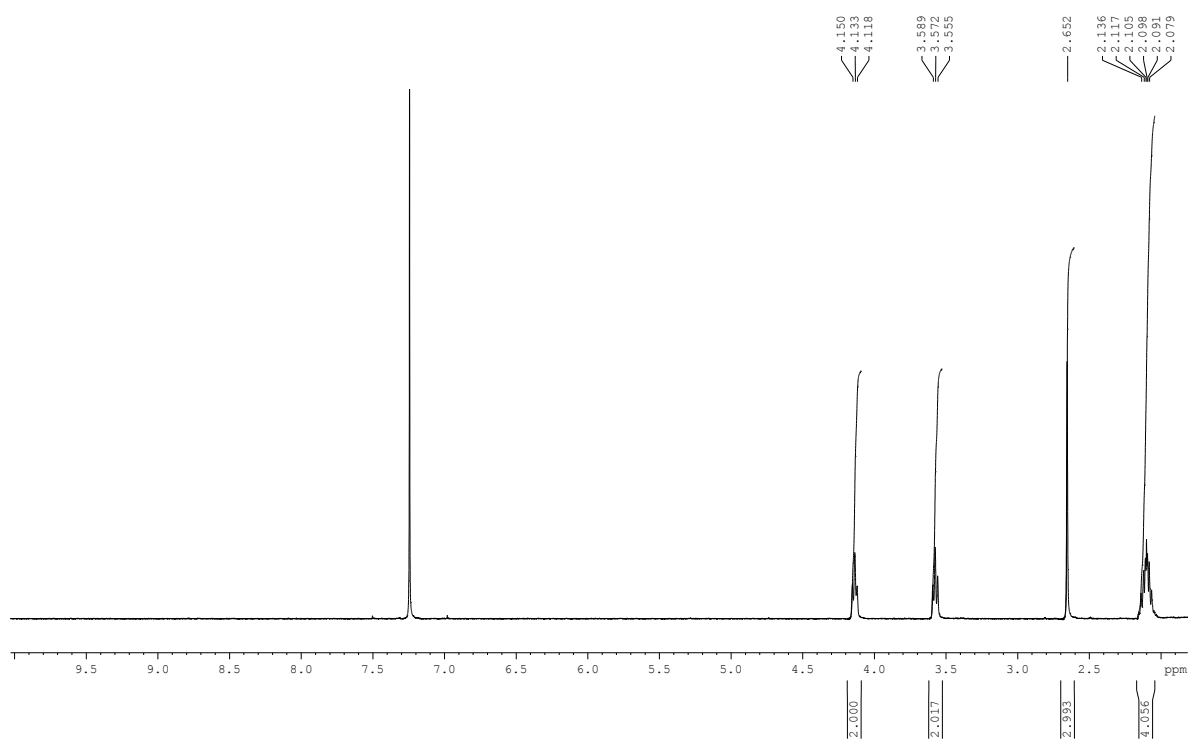


Figure S1. $^1\text{H-NMR}$ spectrum of $[(\text{CO})_5\text{CrC}(\text{NC}_4\text{H}_8)\text{Me}]$ in CDCl_3 .

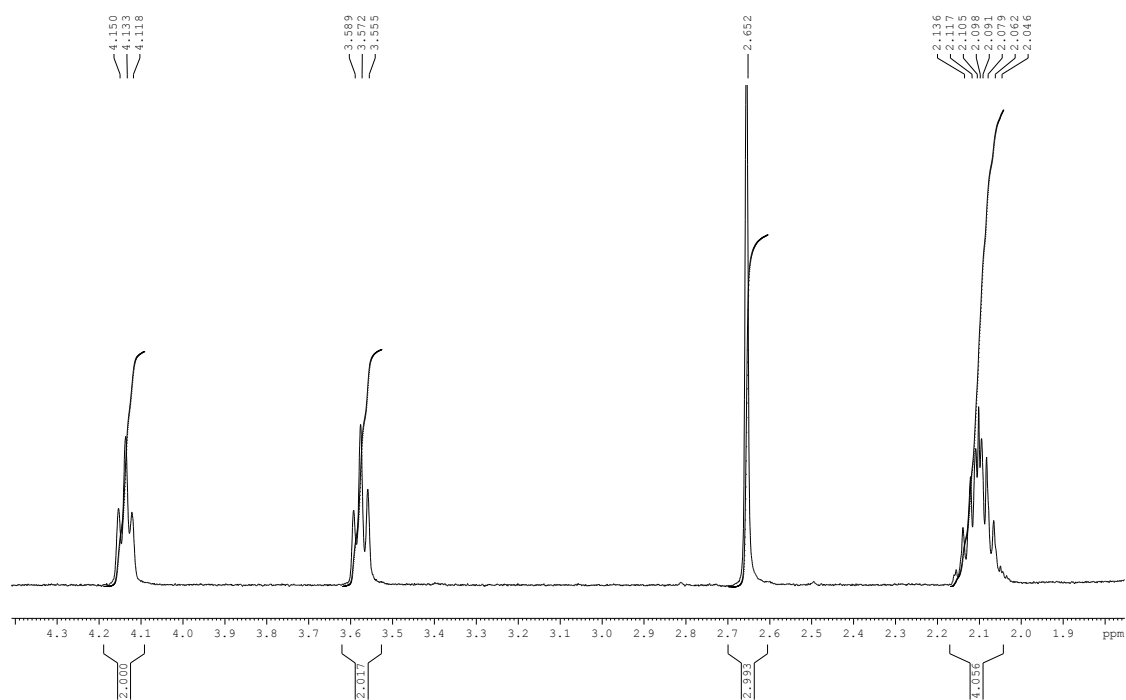


Figure S2. $^1\text{H-NMR}$ spectrum of $[(\text{CO})_5\text{CrC}(\text{NC}_4\text{H}_8)\text{Me}]$ in CDCl_3 .

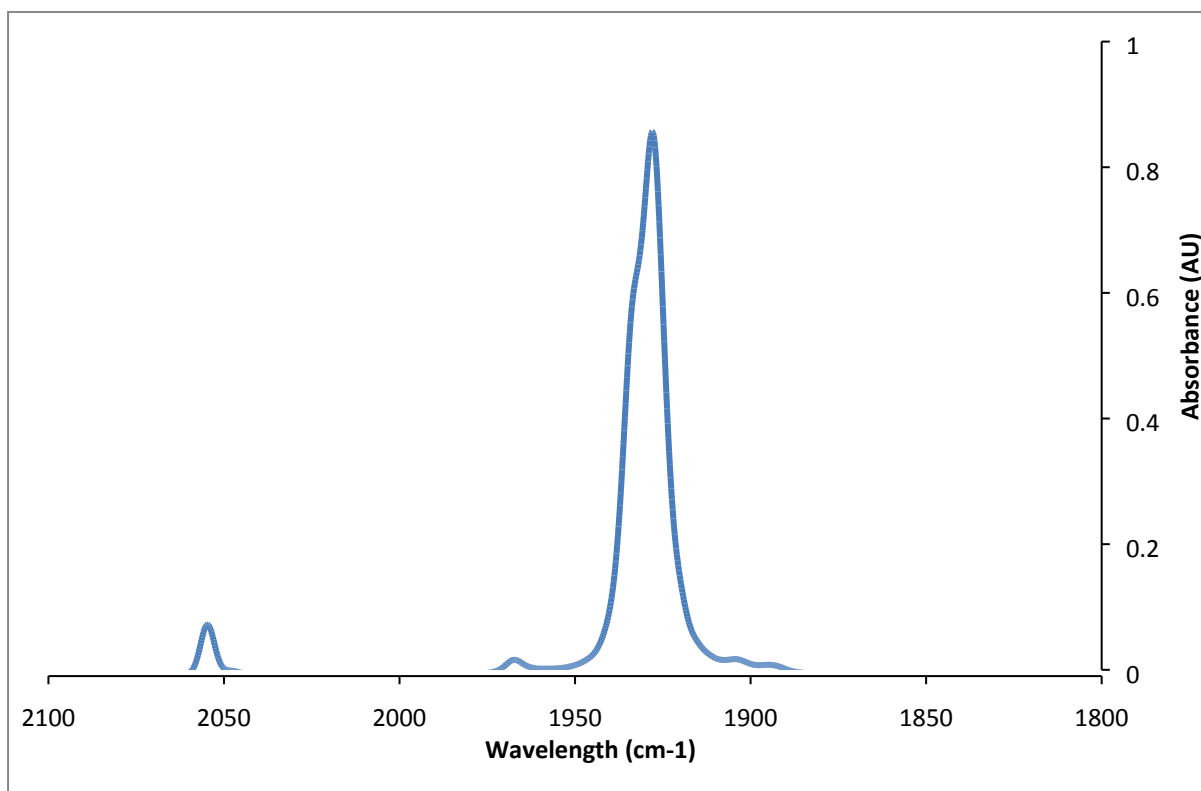


Figure S3. FT-IR spectrum of $[(\text{CO})_5\text{CrC}(\text{NC}_4\text{H}_8)\text{Me}]$ in *n*-heptane.

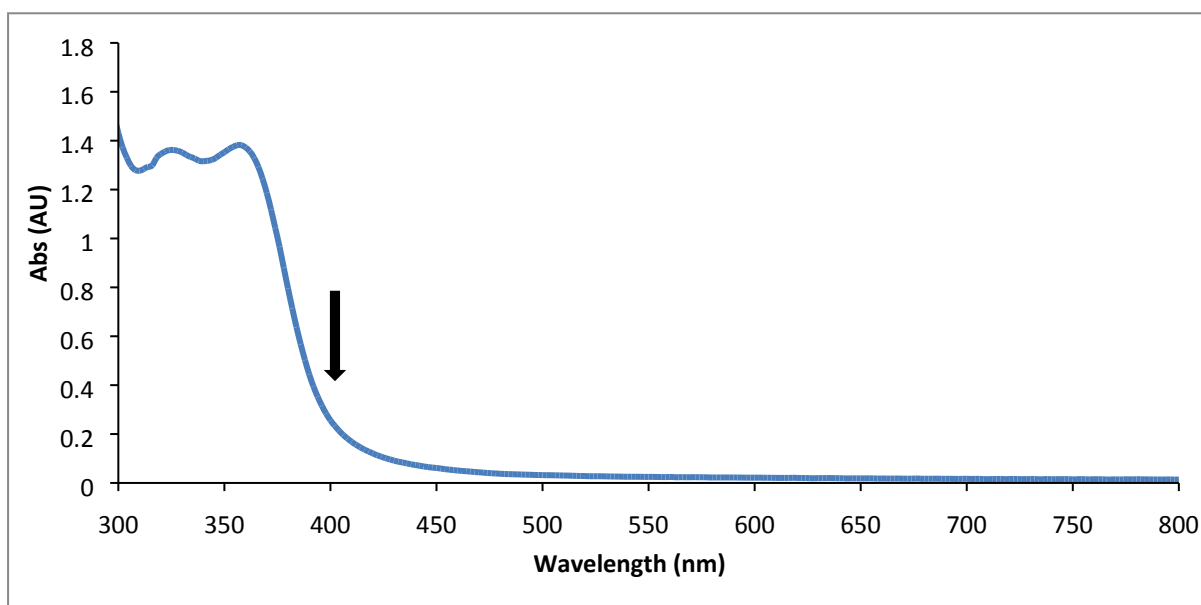


Figure S4. UV-vis spectrum of $[(\text{CO})_5\text{CrC}(\text{NC}_4\text{H}_8)\text{Me}]$ in *n*-heptane.

3. CO Release tests using a myoglobin assay

This procedure was undertaken in the same manner as reported by Motterlini *et al.*³ CO generated from $[(\text{CO})_5\text{CrC}(\text{NC}_4\text{H}_8)\text{Me}]$ was analysed spectrophotometrically by quantifying the conversion of deoxy-myoglobin (deoxy-Mb) to carboxy-myoglobin (Mb-CO). The change in absorbance of the Q-band region of the heme group at a fixed wavelength, 540 nm, was measured to detect the amount of Mb-CO released. The preparation of myoglobin (derived from lyophilised horse heart, 66 μM ; final concentration) was performed by dissolving the protein in phosphate buffered saline (PBS) at a physiological pH (pH 7.4, 0.01 M). 0.1% sodium dithionite was added to reduce the stock Mb to deoxy-Mb. A UV-vis spectrum of this solution (2ml) was recorded and used as a reference standard. The deoxy-Mb solution was then purged with pure CO for 30 minutes to obtain an Mb-CO spectrum. The CO-RM, $[(\text{CO})_5\text{CrC}(\text{NC}_4\text{H}_8)\text{Me}]$, was dissolved in DMSO. A 12 mM solution was prepared. 10 μL aliquots of the CO-RM solutions were added to cuvettes containing 2 mL deoxy-Mb. This was mixed using a pipette and overlaid with a layer of mineral oil (500 μL) to hinder the escape of CO and to prevent the oxygenation of myoglobin (final concentration of the CO-RM; 60 μM). The CO release was measured by photochemical means (355 nm LED) and by thermal means (37 °C).

The spectroscopic data was treated using non-linear regression which included a correction at four isosbestic points. Full details on this procedure has been reported by Fairlamb *et al.*⁴

4. Cyclic Voltammetry and Gas Chromatography

Cyclic Voltammograms (CVs) and bulk electrolysis profiles were recorded in anhydrous acetonitrile (Sigma-Aldrich) with tetrabutylammonium hexafluorophosphate (TBAPF₆), (0.1 M) as a supporting electrolyte. The concentration of the sample was 0.001 M throughout. Experiments were carried out using both a CH Instruments 600A and CH Instruments 750C electrochemical potentiostats (Pico-Amp Booster and Faraday Cage). All electrochemical experiments were performed at room temperature (20°C). A three electrode cell was employed which consisted of a glassy carbon working electrode, a Pt wire auxiliary electrode and a Ag/AgCl reference electrode. The scan rate was 0.1 V s⁻¹ unless otherwise stated. The scan rate dependency of the redox processes was analysed by varying the scan rate from 0.01 V s⁻¹ to 0.05, 0.08, 0.1, 0.5, 0.8, 1.0, 10.0 15.0 and 20.0 V s⁻¹. Cited potentials are referenced relative to the ferrocene/ferrocenium (Fc/Fc⁺) redox couple. The electrochemical cell was deaerated with argon prior to all experiments.

For the bulk electrolysis experiments, deaeration of the solutions with argon prior to the experiment ensured that any CO detected in the headspace resulted from CO-release from the complex. The bulk electrolysis experiments were repeated using a clean glassy carbon electrode in analyte-free electrolyte solution for comparison purposes. A control experiment was also carried out where the complex was dissolved in the electrolyte and kept in the dark with no potential applied. A trace amount of CO was measured from the head space, but this remained constant over the time frame of the experiment. CO-release was detected using a Shimadzu GC-2010 Plus unit (Lab Solutions version 5.57 software) with a dielectric barrier discharge ionization detector (BID) and a ShinCarbon micropacked column with 0.53 mm internal diameter.

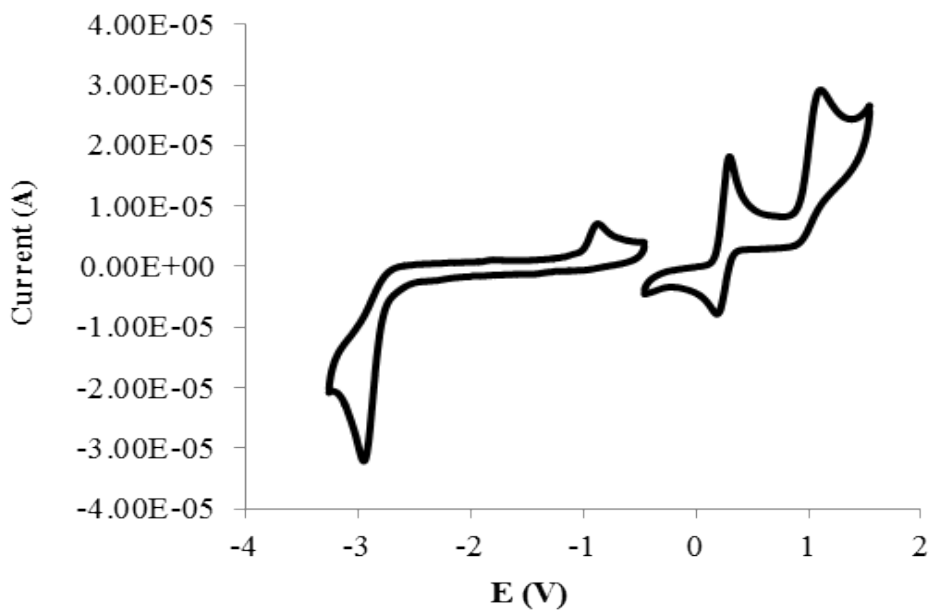


Figure S5 Cyclic voltammogram of oxidation and reduction of $[(\text{CO})_5\text{CrC}(\text{NC}_4\text{H}_8)\text{CH}_3]$ in 0.1M TBAPF₆ in CH₃CN, vs. Fc/Fc⁺. Scan rate = 0.1 V s⁻¹.

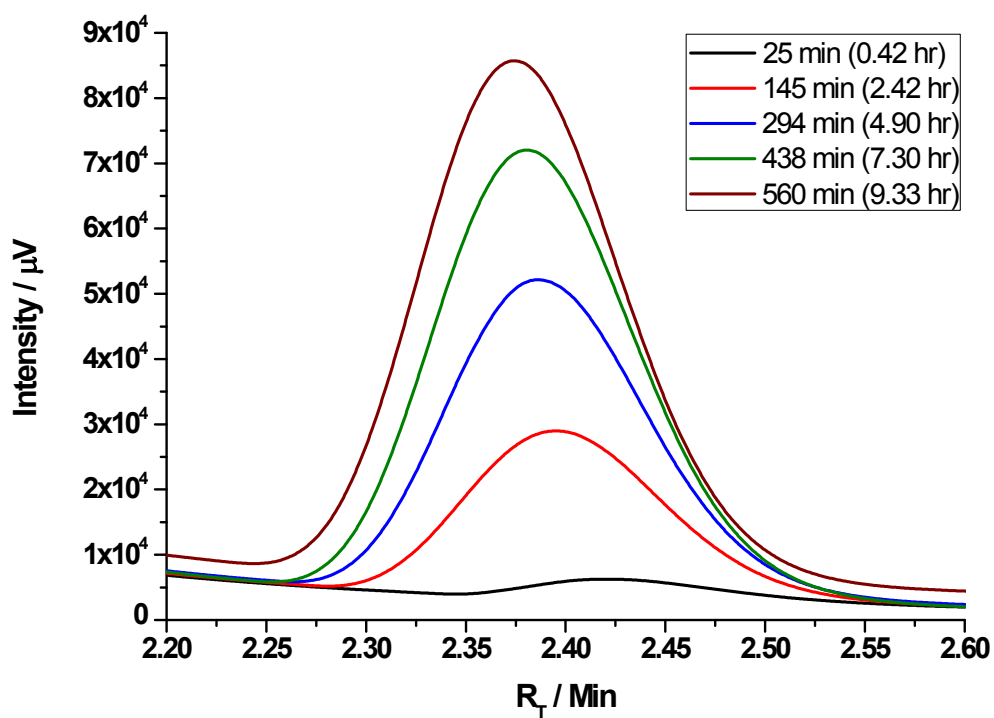


Fig. S6 Gas chromatogram revealing the increase in CO peak area as a result of CO release with time from $[(\text{CO})_5\text{CrC}(\text{NC}_4\text{H}_8)\text{CH}_3]$ under controlled potential electrolysis ($E = +0.36$ V, vs. Fc/Fc⁺).

5. Picosecond Time Resolved Infrared Spectroscopy

The ULTRA laser system used in ps-TRIR studies at the Rutherford Appleton Laboratory is a cryogenically cooled Ti:Sapphire laser amplifier providing 50 fs duration pulses at 10 kHz repetition rate.⁵ The 0.8 mJ, 800 nm output is divided to generate 400 nm pump and mid-IR probe beams through second harmonic generation and difference frequency generation (DFG) of signal and idler generated in an optical parametric amplifier, respectively. The pump beam was attenuated to 0.5 mJ at the sample and focused to overlap with the probe beam in the sample. The pump and probe spot sizes in the sample were 100 and 50 μm , respectively. After the sample, the IR probe beam was dispersed onto two linear 128 element MCT detector arrays acquiring spectra at 10 kHz. The signals from these two detector arrays were then averaged. By modulating the pump laser output at 5 kHz, difference spectra could be generated.⁶ A portion of the IR probe taken before the sample was dispersed on to a second 64 element MCT detector array, which with interpolation was used to generate reference spectra used to remove energy and spectral instabilities of the laser. Samples were contained in flow-through cells with CaF₂ windows with a 500 μm Teflon spacer and rastered to avoid photodegradation of the sample solution.

6. Quantum Chemical Calculations

[(CO)₅CrC(NC₄H₈)Me] Optimised Geometry (B3LYP/Tzvp)

Charge = 0 Multiplicity = 1

C	0	-0.8208	0.9005	-0.05769
C	0	-3.31379	1.12824	-0.03217
C	0	-2.31729	-1.08432	0.0878
C	0	-4.39463	0.08359	0.24145
H	0	-3.43741	1.58049	-1.01921
H	0	-3.29731	1.92841	0.70572
C	0	-3.78364	-1.20646	-0.31338
H	0	-2.16596	-1.40912	1.11861
H	0	-1.64259	-1.64075	-0.55142
H	0	-4.56356	-0.01192	1.31666
H	0	-5.34421	0.34906	-0.22272
H	0	-4.24344	-2.10855	0.08876
H	0	-3.87765	-1.23722	-1.40179
N	0	-2.02333	0.36942	-0.00514
Cr	0	1.08877	-0.07295	0.00602
C	0	2.82381	-0.81934	0.08784
C	0	0.54903	-1.28874	1.3749
C	0	0.63377	-1.32271	-1.36205
C	0	1.69595	1.1098	-1.3705
C	0	1.58246	1.18403	1.36268
O	0	1.89669	1.92401	2.1802
O	0	2.09084	1.7948	-2.20101
O	0	3.87826	-1.27337	0.14006
O	0	0.28509	-2.03222	2.20941
O	0	0.40824	-2.07591	-2.19944
C	0	-0.85962	2.41269	-0.13945
H	0	-1.27365	2.83466	0.78352
H	0	0.12826	2.83695	-0.27553
H	0	-1.49415	2.76076	-0.96122

Molecule: C11H11CrNO5

Details: #p b3lyp/Tzvp SCF=Tight Pop=Full IOp(3/33=1)

Source file: MeFischerCarbeneAOMixPt0.log

Population analysis: MPA

422 orbitals(422 canonical) 74 alpha + 74 beta electrons

Number of fragments: 2

Fragment 1 (11 atoms, 223 orbitals): CrCO5

Fragment 2 (18 atoms, 199 orbitals): Carbene

COMPOSITIONS OF MOLECULAR ORBITALS (GROSS CONTRIBUTIONS, %)
AND OVERLAP POPULATIONS (OP) BETWEEN FRAGMENTS

Alpha MO: 61 62 63 64 65 66 67 68 69 70
HOMO-13 HOMO-12 HOMO-11 HOMO-10 HOMO-9 HOMO-8 HOMO-7
HOMO-6 HOMO-5 HOMO-4
Energy(eV): -11.63 -11.43 -11.19 -11.02 -10.77 -10.70 -10.44 -10.36 -10.05 -8.84
Symmetry: na na na na na na na na na na

FRAG# 1: 68.54 38.13 8.85 93.08 94.62 69.13 2.03 31.01 2.25 2.65
FRAG# 2: 31.46 61.87 91.15 6.92 5.38 30.87 97.97 68.99 97.75 97.35
OP(1 & 2) 0.002 -0.024 -0.010 -0.001 0.000 0.007 -0.016 -0.048 -0.007 0.002

Alpha MO: 71 72 73 74 75 76 77 78 79 80
HOMO-3 HOMO-2 HOMO-1 HOMO LUMO LUMO+1 LUMO+2
LUMO+3 LUMO+4 LUMO+5
Energy(eV): -7.82 -6.17 -5.90 -5.77 -1.33 -0.95 -0.68 -0.56 -0.34 -0.08
Symmetry: na na na na na na na na na na

FRAG# 1: 22.96 99.70 92.44 99.08 19.79 91.91 94.11 99.20 91.78 33.51
FRAG# 2: 77.04 0.30 7.56 0.92 80.21 8.09 5.89 0.80 8.22 66.49
OP(1 & 2) 0.114 -0.006 0.018 -0.041 -0.125 -0.537 -0.039 -0.062 -0.015 -0.416

Alpha MO: 81 82 83 84 85 86 87 88 89 90
LUMO+6 LUMO+7 LUMO+8 LUMO+9 LUMO+10 LUMO+11 LUMO+12
LUMO+13 LUMO+14 LUMO+15
Energy(eV): 0.32 0.34 0.36 0.74 0.79 0.90 0.96 1.01 1.11 1.27
Symmetry: na na na na na na na na na na

FRAG# 1: 99.18 97.15 98.48 48.13 87.98 77.02 51.56 49.03 72.36 71.18
FRAG# 2: 0.82 2.85 1.52 51.87 12.02 22.98 48.44 50.97 27.64 28.82
OP(1 & 2) -0.030 0.002 0.001 -0.568 -1.126 -0.159 -0.031 -0.413 -0.036 -0.186

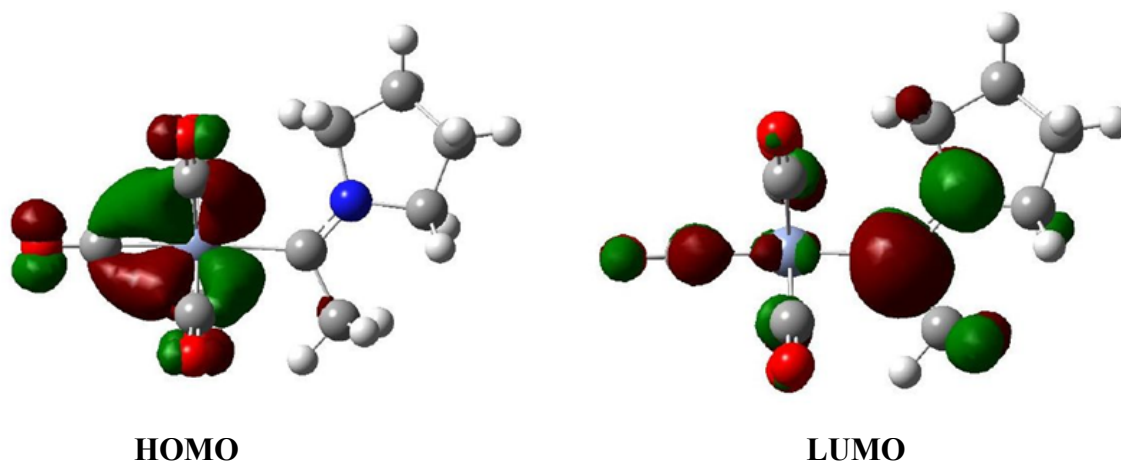


Figure S7. The HOMO and LUMO molecular orbital surfaces for $[(\text{CO})_5\text{CrC}(\text{NC}_4\text{H}_8)\text{CH}_3]$.

Excited state composition (5 lowest energy singlet states) based on single determinant ground state description (TDDFT/B3LYP/Tzvp)

Excited state symmetry could not be determined.

Excited State 1: Singlet-?Sym 3.3369 eV 371.56 nm $f=0.0001$ $\langle S^{*2} \rangle = 0.000$
 74 -> 75 0.70107

This state for optimization and/or second-order correction.

Total Energy, $E(\text{TD-HF/TD-KS}) = -1901.40589297$

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited state symmetry could not be determined.

Excited State 2: Singlet-?Sym 3.7123 eV 333.99 nm $f=0.0114$ $\langle S^{*2} \rangle = 0.000$
 72 -> 75 -0.23483
 72 -> 78 0.18711
 73 -> 75 -0.10435
 74 -> 76 0.60890

Excited state symmetry could not be determined.

Excited State 3: Singlet-?Sym 3.7578 eV 329.93 nm $f=0.0080$ $\langle S^{*2} \rangle = 0.000$
 72 -> 75 0.54018
 73 -> 75 0.19684
 73 -> 76 0.27352
 74 -> 76 0.23172

Excited state symmetry could not be determined.

Excited State 4: Singlet-?Sym 3.7823 eV 327.80 nm $f=0.0740$ $\langle S^{*2} \rangle = 0.000$
 72 -> 75 -0.23169

72 -> 76	0.12991
73 -> 75	0.57718
73 -> 77	-0.21408
74 -> 78	0.13983

Excited state symmetry could not be determined.

Excited State 5: Singlet-?Sym 3.8415 eV 322.75 nm f=0.0011 $\langle S^{*2} \rangle = 0.000$

73 -> 76	-0.12558
73 -> 78	-0.18884
74 -> 77	0.63686
74 -> 78	0.10876
74 -> 83	0.12417

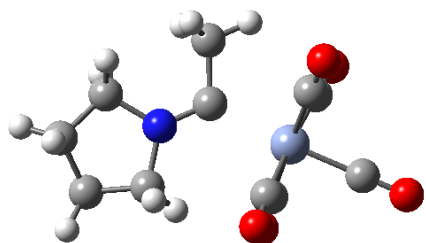


Figure S8. The molecular structure and orientation of $[(\text{CO})_5\text{CrC}(\text{NC}_4\text{H}_8)\text{Me}]$ as used in electron density difference maps in Fig S8 and S9.

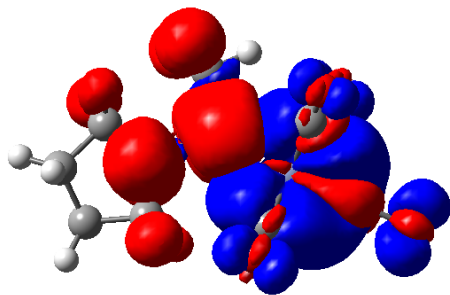


Figure S9. The electron density difference map for the first singlet excited state at the ground state optimised geometry, the blue volumes are the regions where the electron density is reduced in the excited state compared to the ground state and the red volumes are the regions where the electron density is greater in the excited state compared to the ground state. This excited state has substantial metal-to-carbene charge-transfer character (HOMO to LUMO).

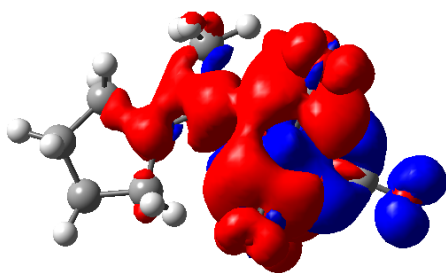


Figure S10. The electron density difference map for the second singlet excited state indicating a greater metal-centred character for this excited state compared to the first singlet excited state (HOMO to LUMO+1)

References

1. J. Connor and E. Fischer, *J. Chem. Soc.*, 1969, A, 578–584.
2. A. Cedillo-Cruz, M. C. Ortega-Alfaro, J. G. López-Cortés, R. A. Toscano, J. G. Penieres-Carrillo, and C. Alvarez-Toledano, *Dalton Trans.*, 2012, **41**, 10568–75.
3. R. Motterlini, *Circ. Res.*, 2002, **90**, 17e–24.
4. A. J. Atkin, J. M. Lynam, B. E. Moulton, P. Sawle, R. Motterlini, N. M. Boyle, M. T. Pryce, and I. J. S. Fairlamb, *Dalton Trans.*, 2011, **40**, 5755–61.
5. G. M. Greetham, Q. Cao, I. P. Clark, P. S. Codd, M. W. George, R. C. Farrow, T. Matousek, A. W. Parker, M. Pollard, D. A. Robinson, Z. J. Xin and M. Towrie, *Appl. Spectrosc.*, 2010, **64**, 1311-1319.
6. M. Towrie, D. C. Grills, J. Dyer, J. A. Weinstein, P. Matousek, R. Barton, P. D. Bailey, N. Subramaniam, W. M. Kwok, C. S. Ma, D. Phillips, A. W. Parker and M. W. George, *Appl. Spectrosc.*, 2003, **57**, 367-380.