# Carbon monoxide and carbon dioxide insertion chemistry of f-block N-heterocyclic carbene complexes

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## Experimental details and characterising data

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### 1.1. General methods and instrumentation

All manipulations were carried out using standard Schlenk line or drybox techniques under an atmosphere of dinitrogen. Protio solvents were degassed by sparging with dinitrogen, dried by passing through a column of activated sieves and stored over potassium mirrors (hexanes, toluene, benzene) or activated 4 Å molecular sieves (thf). Deuterated solvents were dried over potassium ( $C_6D_6$ ,  $C_5D_5N$ ,  $C_4D_8O$ ), distilled under reduced pressure, freeze-pump-thaw degassed three times prior to use.

<sup>1</sup>H NMR spectra were recorded at 298 K, unless otherwise stated, on Bruker DPX 360, AVA 400, DMX 500, AVA 500 or AVA 600 spectrometers and <sup>13</sup>C{<sup>1</sup>H} or <sup>13</sup>C spectra on the same spectrometers at operating frequencies of 90, 100, 125, 125 and 150 MHz respectively. Two dimensional <sup>1</sup>H-<sup>1</sup>H and <sup>13</sup>C-<sup>1</sup>H correlation experiments were used, when necessary, to confirm <sup>1</sup>H and <sup>13</sup>C assignments. All NMR spectra were referenced internally to residual protio solvent (<sup>1</sup>H) or solvent (<sup>13</sup>C) resonances and are reported relative to tetramethylsilane ( $\delta = 0$  ppm). Chemical shifts are quoted in  $\delta$  (ppm) and coupling constants in Hertz.

Mass spectra were recorded by the mass spectrometry service of Edinburgh University's Department of Chemistry. Elemental analyses were carried out at London Metropolitan University and Medac Ltd. Gas chromatographic data were collected using an Agilent Technologies 7890A GC system.

Syntheses of  $Y(L^R)N''_{2,1} Ce(L^R)N''_{2,1} Ce(L^R)_2N''_{1,1}$  and  $U(L^R)N''_{2,2} CeN''_{3,3} UN''_{3,4} UN''_{3,4} CeN''_{3,5} N_2CPh_{2,6}$  were by literature methods.

### 1.2. Syntheses

### 1. CO<sub>2</sub> reactions

### i. Reaction of $U(L^{M})N''_{2}$ with CO<sub>2</sub>; synthesis of $[U(L^{M})N''(OSiMe_{3})(OCNSiMe_{3})]_{n}$

A dark blue solution of  $U(L^M)N''_2$  (540 mg, 0.66 mmol) in hexanes (15 ml) was freeze-pump-thaw degassed then an atmosphere of CO<sub>2</sub> was introduced at room temperature with vigorous stirring. A pale brown solution and precipitate formed immediately, which after 0.5 h changed to a pale green solution and almost colourless precipitate. Following filtration, the solid was washed with hexane (2 x 5 ml) and dried under reduced pressure, affording  $[U(L^M)N''(OSiMe_3)(O=C=NSiMe_3)]_n$  as a very pale green solid (401 mg, 70.3 %).

Found: C 40.29, H 6.79, N 6.41. Calc. for  $C_{29}H_{59}N_4O_3Si_4U$ : C 40.28, H 6.76, N 6.96 %. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>5</sub>N);  $\delta$  52.92 43.52 26.17 15.59 (bs, 2H each, N-CH<sub>2</sub>-CH<sub>2</sub>-N, N-CH<sub>2</sub>-C, Ar-CH), 22.35 10.11 (bs, 6H each, Ar-*o*-CH<sub>3</sub>, C(CH<sub>3</sub>)<sub>2</sub>), 20.40 (bs, 3H, Ar-*p*-CH<sub>3</sub>), the SiMe<sub>3</sub> groups appear as two very broad features in the baseline between  $\delta$  = 6 and -2 ppm. IR (nujol)  $\nu_{max}$ / cm<sup>-1</sup>: 2278(w), 2185(m), 1687(m), 1646(m), 1583(m), 1288(m), 1244(m), 1172(w), 904(m), 836(m), 749(m), 722(m), 680(w). UV  $\lambda_{max}$ / nm ( $\epsilon$ / M<sup>-1</sup> cm<sup>-1</sup>) THF: 601 (20), 809 (9), 999 (22), 1113 (26), 1505 (10) and 1654 (12).

### ii. Reaction of $U(L^{D})N''_{2}$ with $CO_{2}$ ; synthesis of $[U(L^{D})N''(OSiMe_{3})(OCNSiMe_{3})]_{n}$

To a freeze-pump-thaw degassed solution of  $U(L^{D})_2N''$  (0.20 g, 0.24 mmol) in benzene (5 mL) was added CO<sub>2</sub> (1 atm) to afford a brown-green solution. The reaction mixture was stirred for 24 h before the volatiles were removed *in vacuo* to afford  $[U(L^{D})N''(OSiMe_3)(O=C=NSiMe_3)]_n$  as a pale green solid. Yield: 0.053g (32 %). IR (v, nujol mull): 2183 cm<sup>-1</sup>.

### iii. Reaction of $Y(L^{D})N''_{2}$ with $CO_{2}$

To a freeze-pump-thaw degassed solution of  $Y(L^D)_2N''$  (0.011 g, 0.015 mmol) in  $C_6D_6$  (0.5 mL) in a J-Young Teflon valve NMR tube was added CO<sub>2</sub> (1 atm) to afford clear, colourless solution and colourless precipitate immediately. <sup>1</sup>H NMR spectral analysis of the solution showed broad, unassignable resonances across the range 10 – 0 ppm and traces of HL<sup>D</sup>. The solid was isolated by

filtration, dried in vacuo and redissolved in C<sub>5</sub>D<sub>5</sub>N. The <sup>1</sup>H NMR spectrum indicated only the presence of HL<sup>D</sup> and some broad resonances which could not be assigned.

#### Reaction of Ce(L<sup>M</sup>)N"<sub>2</sub> with CO<sub>2</sub> iv.

To an orange freeze-pumped thawed solution of  $Ce(L^{M})N''_{2}$  (15 mg, 0.02 mmol) in  $C_{6}D_{6}$  (0.7 mL) CO<sub>2</sub> was added at room temperature. The colour of the solution turns pale orange/pink. After 12 h an orange solid had precipitated. The precipitate was washed with hexanes and dried in vacuo affording 8 mg of an orange solid that was insoluble in aromatic NMR solvents.

When the reaction is carried out in THF, a yellow precipitate starts to form as soon as the  $CO_2$  is added; no resonances apart from the THF could be seen in the <sup>1</sup>H NMR spectrum. Removal of the THF and addition of pyridine gives a pale yellow solution that shows no resonances in the <sup>1</sup>H NMR spectrum.

#### Reaction of Ce(L<sup>D</sup>)N"<sub>2</sub> with CO<sub>2</sub> ٧.

To a freeze-pump-thaw degassed solution of Ce(L<sup>D</sup>)<sub>2</sub>N" (0.015 g, 0.020 mmol) in C<sub>6</sub>D<sub>6</sub> (0.5 mL) in a J-Young Teflon valve NMR tube was added CO<sub>2</sub> (1 atm) to afford a yellow solution and pale yellow precipitate immediately. <sup>1</sup>H NMR spectral analysis of the solution showed two broad resonances across a range of 10.00 - 0.00 ppm. The solid was isolated by filtration, dried *in vacuo* and redissolved in  $C_5D_5N$ . The <sup>1</sup>H NMR spectrum indicated only HL<sup>D</sup>.

#### Reaction of [Ce(L<sup>M</sup>)<sub>2</sub>N"] with CO<sub>2</sub> vi.

To a yellow freeze-pumped thawed solution of  $Ce(L^{M})_{2}N''$  (7 mg, 0.01 mmol) in THF (0.7 mL)  $CO_{2}$ was added at room temperature. A colourless solid starts to precipitate immediately after addition. Removal of the volatiles in vacuum afforded a vellow solid that was soluble in pyridine gave a pale yellow solution that showed no assignable resonances in the <sup>1</sup>H NMR spectrum.

### 2. COS reactions

#### Reaction of Ce(L<sup>M</sup>)N"<sub>2</sub> with COS vii.

Under the conditions described for the reaction of  $Ce(L^M)_2N''$  with COS, a yellow solution of  $Ce(L^{M})N''_{2}$  was treated with stoichiometric COS. No reaction was observed inder these conditions.

#### Reaction of $Ce(L^{M})_2N''$ with COS; synthesis of $[Ce(L^{M})_2(OSiMe_3)]$ viii.

COS (200 ppm in N<sub>2</sub>) (6L, 0.05 mmol) was bubbled through a yellow solution of  $Ce(L^M)_2N''$  (40 mg, 0.05 mmol) in toluene (5 mL) with a fixed flow regulator (0.5 L/min) for 12 minutes. A pale vellow precipitate formed upon addition. Removal of the volatiles in *vacuo* afforded 38 mg of a pale yellow solid that was insoluble in aromatic NMR solvents and is a mixture of products. An IR spectrum of the afforded product shows a resonance at 2278 cm<sup>-1</sup> which is assigned as the isothiocyanate byproduct Me<sub>3</sub>Si-N=C=S.

IR (nujol);  $\overline{\nu}$  (cm<sup>-1</sup>): 2278 (m).

### 3. CO reactions

### ix. Reaction of $U(L^{D})N''_{2}$ with CO; synthesis of $U(L^{D})N''(OC\{CH_{2}\}SiMe_{2}N\{SiMe_{3}\})$

To a freeze-pump-thaw degassed solution of  $U(L^D)_2N''$  (0.23 g, 0.26 mmol) in benzene (10 mL) was added CO (1 atm). The reaction mixture was heated to 80 °C for 7 days during which time the solution became dark brown in colour. The volatiles were removed *in vacuo* to afford a brow solid. Recrystallisation from toluene at -20 °C afforded  $U(L^D)N''(OC\{CH_2\}SiMe_2N(SiMe_3\})$  as a light brown microcrystalline solid. Yield: 0.16 g, (68 %). Single crystals suitable for an X-ray diffraction



study were grown from a saturated toluene solution at -20 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 360 MHz): xx ppm. Anal. Found (calcd for  $C_{32}H_{64}N_4O_2Si_4U$ ): C, 43.22 (43.32); H, 7.20 (7.27); N, 6.41 (6.31).

### x. Reaction of $Y(L^D)N''_2$ with CO

To a freeze-pump-thaw degassed solution of  $Y(L^D)N''_2$  (0.024 g, 0.034 mmol) in  $C_6D_6$  (0.5 mL) in a J-Young Teflon valve NMR tube was added CO (1 atm) to afford a clear, yellow solution. The <sup>1</sup>H NMR spectrum indicated that no reaction had taken place at room temperature or on heating to 80 °C for 16 h.

### xi. Reaction of $Ce(L^{D})N''_{2}$ with CO

To a freeze-pump-thaw degassed solution of  $Ce(L^D)N''_2$  (0.024 g, 0.031 mmol) in  $C_6D_6$  (0.5 mL) in a J-Young Teflon valve NMR tube was added CO (1 atm) to afford a clear, yellow solution. The <sup>1</sup>H NMR spectrum indicated that no reaction had taken place at room temperature or on heating to 80 °C for 16 h.

### xii. Attempted synthesis of $U(L^{D})N''({CH_2}SiMe_2N(SiMe_3))$

A solution of  $U(L^{D})_{2}N''$  (0.021 g, 0.024 mmol) in  $C_{6}D_{6}$  (0.5 mL) in a J-Young Teflon valve NMR tube was placed under a partial static vacuum and heated to 80 °C for 7 days. The <sup>1</sup>H NMR spectrum indicated  $U(L^{D})_{2}N''$  as the major product, minor new resonances across a range of 86.53 – -68.00 ppm and no resonance corresponding to H<sub>2</sub> were observed.

### xiii. Reaction of UN"<sub>3</sub>CI with CO

To a freeze-pump-thaw degassed solution of UN"<sub>3</sub>Cl (0.009 g, 0.012 mmol) in  $C_6D_6$  (0.5 mL) in a J-Young Teflon valve NMR tube was added CO (1 atm). No reaction was shown to take place at room temperature.

### xiv. Reaction of CeN"<sub>3</sub> with CO

To a freeze-pump-thaw degassed solution of CeN"<sub>3</sub> (0.011 g, 0.018 mmol) in C<sub>6</sub>D<sub>6</sub> (0.5 mL) in a J-Young Teflon valve NMR tube was added CO (1 atm). No reaction was shown to take place at room temperature or on heating to 80 °C for 16 h.

### 4. Ph<sub>2</sub>CN<sub>2</sub> reactions

### xv. Reaction of $U(L^{D})N''_{2}$ with Ph<sub>2</sub>CN<sub>2</sub>; synthesis of $U(L^{D})N''_{2}(NCPh_{2})$

To a solution of  $U(L^D)N''_2$  (0.15 g, 0.17 mmol) in hexanes (10 mL) was added a solution of Ph<sub>2</sub>CN<sub>2</sub> (0.035 g, 0.17 mmol) in hexanes (2 mL) to afford a dark brown solution. The reaction mixture was stirred for 2 h and then the volatiles were removed under reduced pressure to yield a brown solid. Attempted recrystallisation from toluene at -20 °C afforded both pale brown  $U(L^D)N''_2$ (=NCPh<sub>2</sub>) and colourless H<sub>2</sub>NCHPh<sub>2</sub> as diffraction-



quality single crystals which have very similar solubility and thus were not separated by fractional recrystallisation.

### 1.3. Crystallography

X-ray crystallographic data were collected using graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Using the WinGX suite of programs, all structures were solved using direct methods and refined using a full-matrix least square refinement on  $|F|^2$  using SHELXL-97. Unless otherwise stated, all non-hydrogen atoms refined with anisotropic displacement parameters and hydrogen atoms were placed using a riding model. The structural model of U(L<sup>D</sup>)N"(OC{CH<sub>2</sub>} SiMe<sub>2</sub>N{SiMe<sub>3</sub>}) was refined using mild similarity restraints on the displacement ellipsoids of the trimethylsilyl group containing Si1. This structure also contains one molecule of benzene solvent in the asymmetric unit. The benzene was refined using a two part disorder model with an occupancy ratio of 0.546:0.454(14). The carbon atoms of each part were fitted to a regular hexagon and refined isotropically.

	U(L <sup>D</sup> )N"(OC{CH <sub>2</sub> } SiMe <sub>2</sub> N{SiMe <sub>3</sub> })	U(L <sup>D</sup> )N" <sub>2</sub> (NCPh <sub>2</sub> )
Chemical formula	$C_{32}H_{65}N_4O_2Si_4U$	C44H75N5OSi4U 0.5(C6H6)
CCDC number	892962	892963
$M_r$	888.27	1079.53
Crystal system, space group	Triclinic P-1	Monoclinic P21/n
Temperature (K)	100	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.5064(2), 12.1604 (3), 19.8038(4)	13.329(4), 21.293(7), 18.742 (6)
α, β, γ (°)	74.810(1), 77.868(1), 86.530(1)	90, 97.586 (19), 90
$V(\text{\AA}^3)$	2387.20(9)	5272.76(3)
Ζ	2	4
μ (mm <sup>-1</sup> )	3.53	3.21
Crystal shape and colour	Brown plate	Red block
Crystal size (mm)	0.32 x 0.22 x 0.14	0.26 x 0.10 x 0.06
<b>Radiation type</b>	Μο <i>Κ</i> α	Μο Κα
Diffractometer	Bruker SMART APEX CCD area detector	Bruker <i>SMART</i> <i>APEX</i> CCD area detector
Scan method	$\omega$ and $\phi$ scans	$\omega$ and $\phi$ scans
	SI 5	

Absorption correction	Multi-scan SADABS	Multi-scan SADABS
$\theta_{max}, \theta_{min}$ (°)	30.5, 1.7	26.4, 1.8
T <sub>min</sub> , T <sub>max</sub>	0.3365, 0.4330	0.5837, 0.7454
Number of measured, independent and observed [I > 2s(I)] reflections	39388, 13332, 12491	67958, 10820, 9337
<b>R</b> <sub>int</sub>	0.039	0.067
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.057, 0.165, 1.57	0.042, 0.102, 1.04
Number of reflections	13332	10820
Number of parameters	405	541
Number of restraints	0	0
H atom treatment	Riding	Riding
$(\Delta/\sigma)_{\rm max}$	0.001	< 0.001
$\Delta \rho_{max}, \Delta \rho_{min} \ (e {\rm \AA}^{-3})$	4.90, -1.89	2.89, -1.11

### 1.4. References

- 1. P. L. Arnold, I. J. Casely, Z. R. Turner and C D. Carmichael, *Chem. Eur. J.*, 2008, 14, 10415-10422.
- 2. Z. R. Turner, R. Bellabarba, R. P. Tooze and P. L. Arnold, J. Am. Chem. Soc., 2010, 132, 4050-4051.
- 3. D. C. Bradley, J. S. Ghotra and F. A. Hart, J. Chem. Soc., Dalton Trans., 1973, 1021-1023.
- 4. L. R. Avens, S. G. Bott, D. L. Clark, A. P. Sattelberger, J. G. Watkin and B. D. Zwick, *Inorg. Chem.*, 1994, **33**, 2248-2256.
- 5. H. W. Turner, R. A. Andersen, A. Zalkin and D. H. Templeton, *Inorg. Chem.*, 1979, **18**, 1221-1224.
- 6. K. Nakagawa, H. Onoue and K. Minami, Chem. Commun., 1966, 730-731.