Carbon monoxide coupling and functionalisation at a simple uranium coordination complex

Supplementary data: Experimental details and characterising data

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General Details

All manipulations were carried out under a dry, oxygen-free dinitrogen atmosphere using standard Schlenk techniques or in an MBraun Unilab glovebox unless otherwise stated. Other solvents were degassed by N_2 purge then dried by passage through activated alumina towers prior to use. All deuterated solvents were freeze-pump-thaw degassed three times, boiled over potassium (apart from $CDCl_3$ which was boiled over CaH_2) and vacuum transferred prior to use. The compound $[U\{N(SiMe_3)_2\}_3]$ was made according to a literature procedure[1], or in a slight modification, from UI_3[2]. Elemental analyses were determined by Mr. Stephen Boyer at London Metropolitan University. ^1H NMR spectra were recorded on a Bruker DPX 500 spectrometer or Bruker AVA 600 spectrometer, operating at 500.13 MHz or 599.81 MHz, ^2H NMR spectra on the same spectrometers at 76.77 and 92.07 MHz, and $^{13}C\{^1H\}$ on a Bruker AVA 400 spectrometer at 100.57 MHz, respectively at 298 K. Chemical shifts are reported in parts per million, and referenced to residual proton resonances calibrated against external TMS. Infrared spectra were recorded on Jasco 410 spectrophotometer, w = weak, m = medium, s = strong intensity.

Abbreviations

$N'' = N(SiMe_3)_2$; $Si' = SiMe_3$; $BAr^F{}_3 = B(C_6F_5)_3$; 9-BBN = 9-bora-bicyclononane.

$N''_3UOCCOUN''_3$ 1

$N''_3U{-}O{-}C{\equiv}C{-}O{-}UN''_3$

Method a. To a freeze-pump-thaw degassed solution of UN''_3 (1.00 g, 1.39 mmol) in toluene (20 mL) was added CO (1 atm) at room temperature. After 1 hour, golden-coloured microcrystalline solid started to precipitate and the reaction mixture was then kept at room temperature for 3 days. The solid was isolated by filtration, washed with hexane (3 x 10 mL) and then dried *in vacuo* to afford $N''_3UOCCOUN''_3$ as a golden-coloured solid. Yield 0.853 g (82 %).

Method b.

To a freeze-pump-thaw degassed solution of UN''_3 (0.0487 g, 0.0677 mmol) in hexane (2 mL) was added CO (1 atm) at room temperature. After 15 minutes, golden coloured microcrystalline solid started to precipitate and the reaction mixture was then kept at room temperature for 3 days. The solid was isolated by filtration, washed with hexane (3 x 1 mL) and then dried *in vacuo* to afford $N''_3UOCCOUN''_3$ as a golden solid. Yield 0.292 g (58 %).

No reaction was observed when the reaction was repeated in either THF or pyridine.

Single crystals suitable for an X-ray diffraction study were grown from C_6D_6 solution at room temperature. ^1H NMR (C_6D_6, 599.8 MHz, 298 K): - 8.55 (108 H, s, $N\{Si(CH_3)_3\}_2$) (fwhm = 1297 Hz) ppm. Anal. Found (calcd for $C_{38}H_{108}N_6O_2Si_{12}U_2$): C, 30.37 (30.54); H, 7.35(7.28); N, 5.55 (5.62). IR (ν, nujol mull): 2478 (vw), 2214 (vw), 2083 (vw), 1921 (w), 1856 (w), 1400 (s), 1359 (2) 1289 (m), 1250 (s) 930 (s), 835 (s), 769 (s), 670 (m), 654 (m), 609 (s), 502 (vw) cm^{-1}.

The IR spectrum contains one very small absorption in the region anticipated for a C≡C bond, at 2214 cm^{-1} is the $^{12}C{\equiv}^{12}C$ stretch, then the diatomic molecule relationship predicts a $^{13}C{\equiv}^{13}C$ band at 2127 cm^{-1} (but only one at 2154 cm^{-1} is observed). It is reasonable that these small bands are artefacts and this symmetrical stretch is simply not observed by IR spectroscopy (see also reference 3). The two spectra are shown overlaid in figure SI.1.

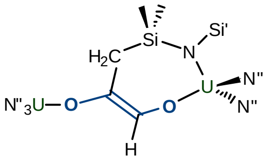
$N''_3UO^{13}C^{13}COUN''_3$ 1a

$N''_3U{-}O{-}^{13}C{\equiv}^{13}C{-}O{-}UN''_3$

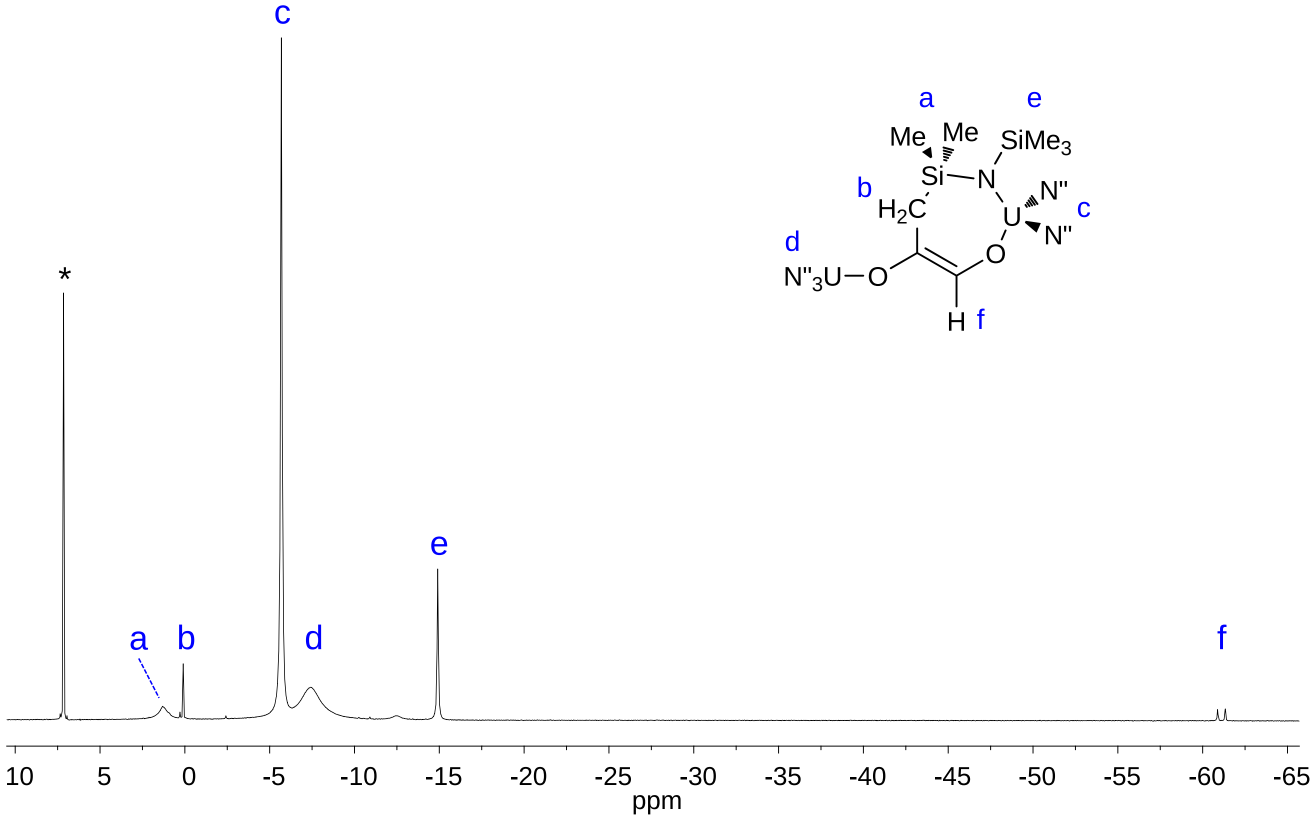
To a freeze-pump-thaw degassed solution of UN''_3 (0.0502 g, 0.0698 mmol) in toluene (2 mL) was added ^{13}CO (1 atm) at room temperature. After 1 hour, golden coloured microcrystalline solid started to precipitate and the reaction mixture was then kept at room temperature for 3 days. The solid was isolated by filtration, washed with hexane (3 x 2 mL) and then dried *in vacuo* to afford $N''_3UO^{13}C^{13}COUN''_3$ as a golden-coloured solid. ^1H NMR (C_6D_6, 599.8 MHz, 298 K): -8.55 (108

H, s, $N\{Si(CH_3)_3\}_2$) ppm. $^{13}C\{^1H\}$ (C_6D_6, 151 MHz, 298 K) 171.0 ($O^{13}C^{13}CO$) ppm. The resonance associated with the $N\{Si(CH_3)_3\}_2$ carbon was not visible in the spectrum. Anal. Found (calcd for $C_{38}H_{108}N_6O_2Si_{12}U_2$): C, 30.12 (30.54); H, 6.79 (7.28); N, 5.05 (5.62) IR (ν, nujol mull): 2478 (vw), 2154 (vw), 2082 (vw), 1921 (vw), 1856 (vw), 1332 (s), 1250 (s), 1156 (vw), 930 (s), 836 (s), 770 (s0, 734 (m), 672 (m), 656 (m), 610 (s), 505 (vw) cm^{-1}.

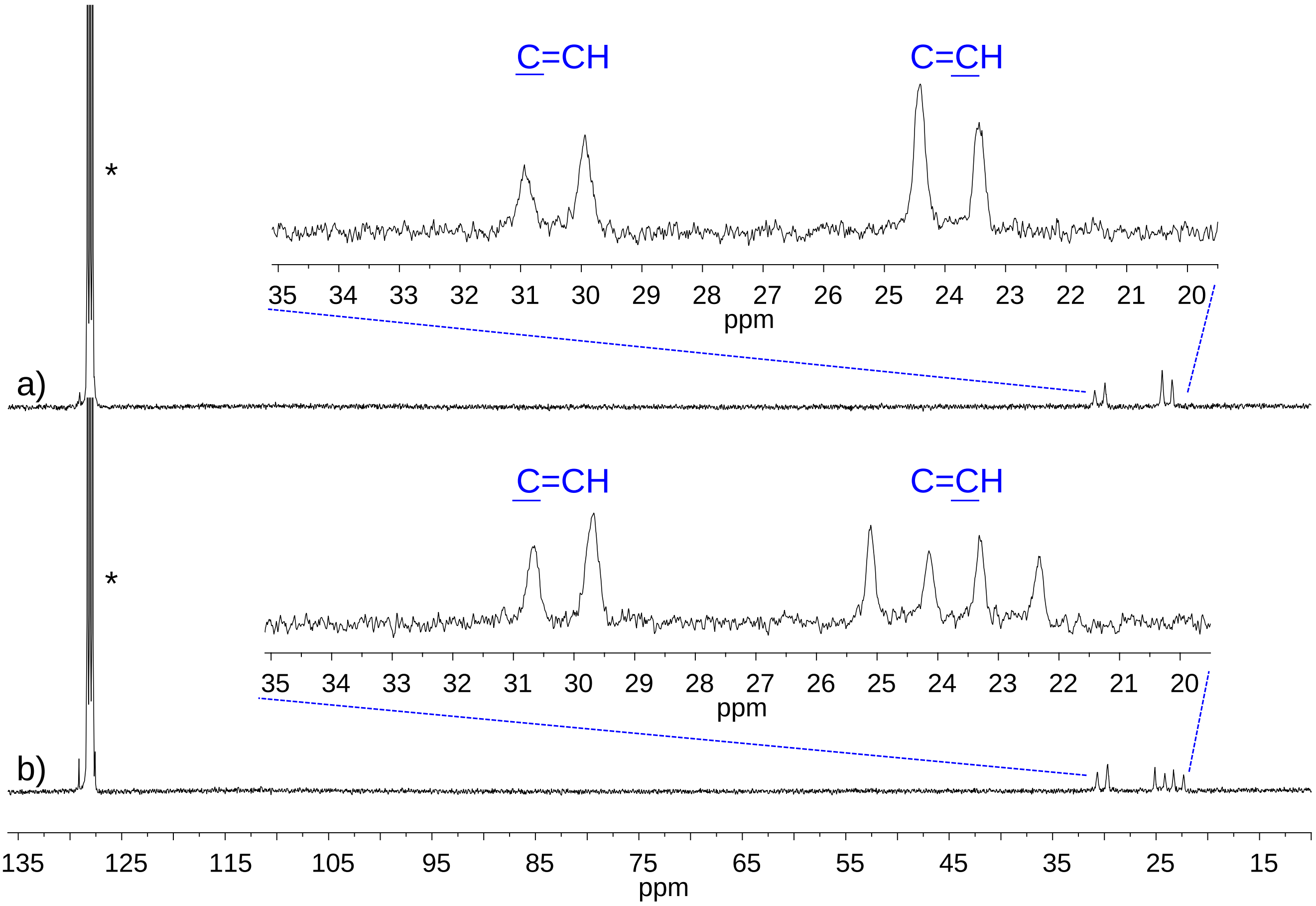
$N''_3UOC=C(H)OU\{N(SiMe_2CH_2)(SiMe_3)\}N''_2$ 2



A slurry of $N''_3UOCCOUN''_3$ (0.107 g, 0.0716 mmol) in toluene (10 mL) was heated to 80 ºC for 24 h. The volatiles were removed under reduced pressure to afford $N''_3UOC=C(H)OU\{N(SiMe_2CH_2)(SiMe_3)\}N''_2$ as a golden-coloured solid. Yield 0.0713 g (67 %) ^1H NMR (C_6D_6, 599.8, MHz, 298 K): 1.32 (6 H, s, $N\{Si(CH_3)_3\}Si(C\underline{H}_3)_2$, 0.10 (1 H, s, $CHC\underline{H}_2$), -5.66 (36 H, s, $U[N\{Si(CH_3)_3\}_2]_2$), -7.47 (54 H, s, $U[N\{Si(CH_3)_3\}_2]_3$), -14.85 (9 H, s, $N\{Si(CH_3)_3\}$), -60.70 (1 H, s, $C\underline{H}CH_2$) ppm. IR (ν, KBr): 2954 (m), 2897 (m) 2799 (w), 1634 (m), 1410 (w), 1357 (w), 1248 (s), 1183 (w), 1099 (m) ,1051(m), 930 (s), 838 (s), 792 (m), 645 (w) cm^{-1}.



^{1}H NMR spectrum (C_6D_6, 298 K, 400 MHz) of N''$_3$UOC=C(H)OU{N(SiMe$_2$CH$_2$)(SiMe$_3$)}N''$_2$ '*' indicates residual protio solvent.



a) $^{13}C\{^1H\}$ NMR spectrum (C_6D_6. 298 K, 400 MHz) and b) ^{13}C NMR spectrum of $N''_3UO^{13}C{=}^{13}C(H)OU\{N(SiMe_2CH_2)(SiMe_3)\}N''_2$. '*' indicates solvent

$N''_3UOC{=}C(H)OU\{N(SiMe_2CH_2)(SiMe_3)\}N''_2$: $N''_3UOCCOUN''_3$ 1:1

A slurry of $N''_3UOCCOUN''_3$ (0.151 g, 0.101 mmol) in toluene (10 mL) was heated to 80 ºC for 5.5 h. The clear orange solution was cooled slowly to room temperature to afford single crystals suitable for an X-ray diffraction study. The study confirmed the contents of the crystal to be a 1:1 co-crystal of $N''_3UOC{=}C(H)OU\{N(SiMe_2CH_2)(SiMe_3)\}N''_2$: $N''_3UOCCOUN''_3$. This was confirmed by solution ^1H NMR spectroscopy of a sample of isolated single crystals. Yield 0.122 g (81 %).

Reaction of $N''_3UOC{\equiv}COUN''_3$ with BAr^F_3

$N''_3UOC{\equiv}COUN''_3$ (0.024 g, 0.016 mmol) and BAr^F_3 (0.016 g, 0.032 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube. No reaction was shown to have taken place by

^{1}H NMR spectroscopy at room temperature. Single crystals formed were shown to be N"$_3$UOC≡COUN"$_3$ by inspection of the unit cell parameters.

Reaction of N"$_3$UOC≡COUN"$_3$ with 9-BBN

N"$_3$UOC≡COUN"$_3$ (0.010 g, 0.0070 mmol) and 9-BBN (0.0017 g, 0.0070 mmol) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube to afford a pale brown solution and a brown solid. The ^{1}H NMR spectrum indicated mainly unreacted 9-BBN and N"$_3$UOC≡COUN"$_3$ with the appearance of two small resonances. ^{1}H NMR (C_6D_6, 250 MHz): 3.00 – 0.90 (overlapping m, 9-BBN), 2.50 (s), 2.95 (s), -8.71 (s, N{Si(CH$_3$)$_3$}$_2$) ppm. Relative integrations could not be accurately recorded due to the turbidity and precipitation of material from the solution. Single crystals grown within in the solution were shown to be N"$_3$UOC≡COUN"$_3$ by analysis of the unit cell metrical parameters.

Reaction of N"$_3$UOC≡COUN"$_3$ with (*B*-I)-9-BBN

N"$_3$UOC≡COUN"$_3$ (0.023 g, 0.016 mmol) and (*B*-I)-9-BBN (31 μL, 0.0031 mmol, 1.0 M in hexanes) were combined in C_6D_6 (0.5 mL) in a J-Young Teflon valve NMR tube. The ^{1}H NMR spectrum indicated mainly unreacted (*B*-I)-9-BBN and N"$_3$UOC≡COUN"$_3$ and the appearance on one new small resonance. ^{1}H NMR (C_6D_6, 400 MHz): -0.98, 2.50 – 0.50 (overlapping m, (*B*-I)-9-BBN), -8.55 (s, N{Si(CH$_3$)$_3$}$_2$) ppm. Relative integrations could not be accurately recorded due to the turbidity and precipitation of material from the solution. Single crystals grown within in the solution were shown to be N"$_3$UOC≡COUN"$_3$ by analysis of the unit cell metrical parameters.

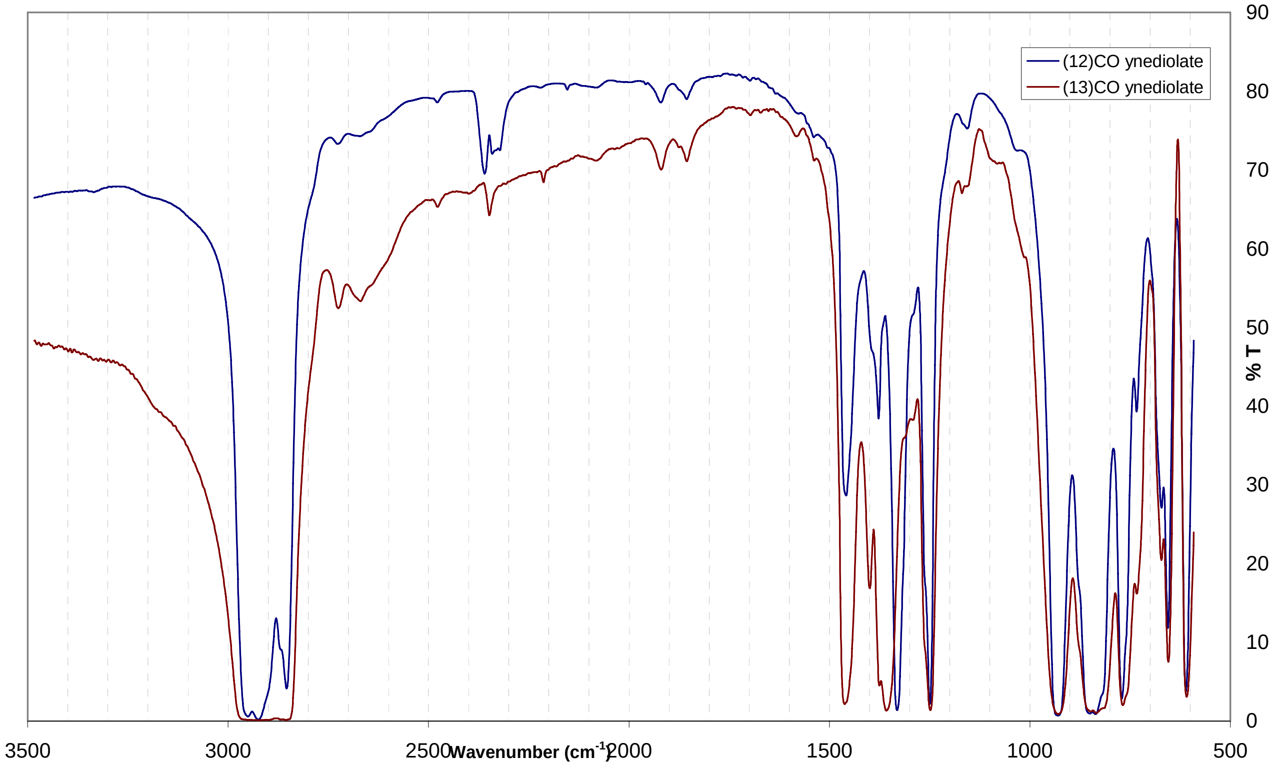


Figure SI1 FTIR spectra of **1** and **1a**, nujol mull

Crystallographic Details

Crystallographic X-ray data were collected using Mo-K$_\alpha$ radiation (λ = 0.71073) on a Bruker SMART APEX and an Oxford Diffraction Excalibur CCD area detector diffractometer using ω scans. Structure solution and refinement was carried out using the WinGX32 suite of programs. X-ray crystallographic coordinates for the complexes have been deposited at the Cambridge Crystallographic Database, numbers 775504 and 775505.

Crystallographic data summary table

	po8091_N3UOCCOUN3	p10006_N3UOCHCROUN2andN3UOCCOUN3inasymunit
Crystal data		
Chemical formula	$C_{38}H_{108}N_6O_2Si_{12}U_2 \cdot 3(C_6H_6)$	$C_{57}H_{162}N_9O_3Si_{18}U_3$
M_r	1728.77	2241.67
Crystal system, space group	Triclinic, $P\bar{1}$	Monoclinic, $P12_1/c1$
Temperature (K)	150	170
a, b, c (Å)	11.0022 (5), 11.7354 (6), 18.0634 (10)	30.0251 (6), 15.6531 (3), 22.4759 (4)
α, β, γ (°)	90.254 (3), 94.779 (3), 117.609 (3)	90, 103.691 (2), 90
V (Å^3)	2057.05 (18)	10263.2 (3)

Z	1	4
μ (mm^{-1})	4.14	4.97
Crystal size (mm)	0.39 × 0.17 × 0.13	0.22 × 0.16 × 0.14
Data collection		
Diffractometer	Bruker *SMART APEX* CCD area detector diffractometer	Xcalibur, Eos diffractometer
Absorption correction	Multi-scan *SADABS*	Multi-scan CrysAlisPro[a]
$T_{\min}$, $T_{\max}$	0.295, 0.615	0.811, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	24088, 9326, 8936	57493, 22833, 14064
R_{int}	0.026	0.032
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.030, 0.067, 1.20	0.065, 0.175, 1.08
No. of reflections	9326	23909
No. of parameters	370	863
No. of restraints	0	1
H-atom treatment	Riding	mixture of independent and constrained refinement
$\Delta\rangle_{\max}$, $\Delta\rangle_{\min}$ (e Å^{-3})	2.24, -0.93	8.54, -4.67

a. Oxford Diffraction Ltd., Version 1.171.33.55 (release 05-01-2010 CrysAlis171 .NET) (compiled Jan 5 2010,16:28:46) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

References

1. L. R. Avens, S. G. Bott, D. L. Clark, A. P. Sattelberger, J. G. Watkin and B. D. Zwick, *Inorg. Chem.*, 1994, **33**, 2248.
2. C. D. Carmichael, N. A. Jones and P. L. Arnold, *Inorg. Chem.*, 2008, **47**, 8577.
3. A. S. Frey, F. G. N. Cloke, P. B. Hitchcock, I. J. Day, J. C. Green and G. Aitken, *J. Am. Chem. Soc.*, 2008, **130**, 13816.