Carbon Nitride as a Ligand: Edge Site Coordination of ReCl(CO)₃-fragments to $g-C_3N_4$

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Electronic Supplementary Information

Experimental

General: Urea (\geq 99.5%), and ammonia in ethanol (Sigma-Aldrich), 5, 7-dimethyl-[1, 8]-naphthyridine-2-amine (DMNA) (Santa Cruz Biotechnology), rhenium carbonyl (Fluorochem) were used without further purification. Toluene was dried using an Innovative Technology PureSolv Solvent Purification System and Ethanol dried using activated molecular sieves (4 Å). Water was purified using a Millipore system. [ReCl(CO)₅] was synthesised using a literature method.¹

Characterisation: ¹³C solid-state CP-MAS NMR spectra were collected using a Bruker Ascend 400 WB NMR spectrometer. ¹H and ¹³C solution NMR spectra were recorded using a Bruker AV500B (500 MHz) spectrometer and peaks referenced to residual solvent. ATR and solution IR spectra were recorded using a PerkinElmer FT-IR Spectrum Two spectrometer. DRIFTS spectra were collected after diluting samples in KBr and using a Bruker Equinox 55 spectrometer. PXRD diffractograms were collected on a Bruker D8 X-ray diffractometer with a Lynxeye detector and using Cu Ka radiation collected with a step size of $0.02^{\circ} 2\theta$ and each data point for 0.2s. SEM images were collected using a JSM 7800F Prime Field Emission Scanning Electron Microscope. Samples for SEM were mounted onto an aluminium stub using conductive carbon tape and coated with Pd/Pt (10 nm) using a JEOL JFC 2300 HR High Resolution Fine Coater. CHN analyses were carried out using an Exeter Analytical Inc CE-440 analyser. For chlorine analysis, samples were combusted using the oxygen flask technique. Ion chromatography on a Dionex Aquion Chromatography system fitted with an IonPac AS22 anion exchange column was used to analyse combustion products. Mass spectrometry was collected using a Bruker microTOF Electrospray (ESI) mass spectrometer. XPS measurements were taken using a Kratos Axis Supra using a monochromated Al-ray anode (1486.69 eV) and fitted with a charge neutraliser. All measurements were performed with a pressure of <10⁸ Torr. Wide scans were performed using a pass energy of 160 and step size of 1 eV and high resolution scans with a pass energy of 20 and step size of 0.1 eV. Data was analysed using CASAXPS v2.3.15. C 1s, O 1s and N 1s peaks were fit using a GL(30) line shape. Re 4f peaks were fitted using a DS(0.01,400)GL(30) line shape and a doublet separation of 2.43 eV. All spectra were charge corrected to adventitious carbon at 284.8 eV. High Angle Annular Dark field (HAADF) images were acquired using a double aberration corrected 200 keV JEOL 2200FS (Scanning)/Transmission Electron Microscope (S)TEM with a field emission gun equipped with a Thermo Scientific Noran 7 Energy Dispersive X-ray (EDX) detection system. Sample preparation for TEM analysis was done by crushing a few grains of the sample between two microscope glass slides and dusting with powder holey carbon films supported by 300 mesh TEM Cu grids (Agar scientific, S147-3).

Single crystals of [ReCl(CO)₃(DMNA- $\kappa^2 N$, N')] were grown by vapour diffusion of pentane into saturated solution in acetone. Diffraction data were collected at 110 K, on an Oxford Diffraction SuperNova diffractometer with Mo-K radiation ($\lambda = 0.71073$ Å) using an EOS CCD camera. The crystal was cooled with an Oxford Instruments Cryojet. Diffractometer control, data collection, initial unit cell determination, frame integration and unit-cell refinement was carried out with "Crysalis". Faceindexed absorption corrections were applied using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. OLEX2 was used for overall structure solution, refinement and preparation of computer graphics and publication data. Within OLEX2, the algorithms used for structure solution were ShelXT dual-space. Refinement by full-matrix least-squares used the SHELXL-97 h algorithm within OLEX2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using a "riding model" and included in the refinement at calculated positions.

Synthesis of g-C₃N₄: Urea (31 g, 0.52 mol) was placed in a ceramic crucible, covered with a lid and heated to 550 °C in air (ramp rate of 5°C / min) for 180 min to give raw g-C₃N₄ (1.93 g) as a pale yellow powder. Raw g-C₃N₄ (500 mg) was then placed in a Schlenk tube under nitrogen before addition of ammonia in ethanol (2 mol dm⁻³, 20 mL). The mixture was stirred for 3 hrs before isolation by filtration. Base treated g-C₃N₄ was then washed with ethanol (3 x 10 mL), water (3 x 10 mL), then ethanol (3 x 10 mL) and dried at 80 °C overnight to give g-C₃N₄ as a pale yellow powder. ¹³C CP-MAS NMR (10 kHz, 300K, ppm, Ref. Adamantane, 29.5 ppm): δ = 164, 156 IR (ATR, cm⁻¹): 3164, 1621, 1557, 1416, 1321, 1240, 1151, 806, 557. Elemental analysis (CHN): Calculated for C₃N₄: C, 39.14; H, 0; N, 60.86. Found C, 33.74; H, 1.754; N, 59.57. Formula: C₃N₄sH_{1.86}

Synthesis of [ReCl(CO)₃(g-C₃N₄)]: Base-treated g-C₃N₄ (700 mg, 3.53 mmol) was placed in Schlenk tube and heated at 110 °C under vacuum for 2 hr. [Re(CO)₅Cl] (150 mg, 0.42 mmol) dissolved in dry toluene (20 mL) was transferred under nitrogen to g-C₃N₄ and the mixture refluxed under nitrogen for 21 hrs before cooling. The resulting solid was isolated by filtration, washed with toluene (3 x 60 mL) and dried at 80 °C to give [ReCl(CO)₃(g-C₃N₄)] a fine orange powder . Yield: 550 mg, 79 %.

Elemental analysis: Calculated for [(ReCl(CO)₃)_{0.07}(g-C₃N₄)]: C, 39.14, H, O, N, 60.86. Found C, 31.70; H, 1.87; N, 54.73; Cl, 1.17; Re, 7.34. Formula [($C_{3.07}N_{4.54}H_{2.15}Cl_{0.038}Re_{0.045}$)] (normalized to the nitrogen content found for g-C₃N₄).

Leaching study of [ReCl(CO)₃(g-C₃N₄)]: [ReCl(CO)₃(g-C₃N₄)] (30 mg) was stirred in 2 mL solvent for 3 hrs followed by filtration of a 1 mL portion of the suspension, which was analysed using liquid IR

spectroscopy. The remaining [ReCl(CO)₃(g-C₃N₄)] suspension was filtered and washed with solvent (3 x 2 mL) before drying for 2 hrs at 60 °C and analysed using ATR-IR spectroscopy.

Synthesis of $[Re(CO)_3Cl(DMNA)]$: $[Re(CO)_5Cl]$ (100 mg, 0.28 mmol) was placed into a Schlenk flask and dissolved in toluene (20 mL) under nitrogen. 5, 7-dimethyl[1,8]naphthyridin-2-amine (48 mg, 0.28 mmol) was placed in a Schlenk flask under nitrogen and dissolved in DMF (3 mL). The $[Re(CO)_5Cl]$ solution was transferred to the DMNA solution and stirred at 90 °C for 1 hr. When the solution infrared spectrum of the reaction mixture showed full conversion, the volume of the solvent was reduced to ca. 2 mL *in vacuo*, the solution cooled and diethyl ether (35 mL) added. The resulting precipitate was isolated by filtration and washed with diethyl ether (3 x 5 mL). $[Re(CO)_3Cl(DMNA)]$ was dried *in vacuo* and stored in a glovebox. Single crystals of $[Re(CO)_3Cl(DMNA)]$ were grown for crystallography by vapour diffusion of pentane into a saturated acetone solution of $[Re(CO)_3Cl(DMNA)]$. The product is an ivory microcrystalline solid. Yield: 68 mg, 50 %.

¹H NMR (500 MHz, d₃-MeCN, 25 °C / ppm): δ = 8.08 (d, 9.2 Hz, 1H, CH), 7.15 (d, 9.2 Hz, 1H, CH), 7.08, (s, 1H, CH), 5.77 (br s, 2H, NH₂), 2.97 (s, 3H, CH₃), 2.89 (s, 3H, CH₃)

¹³C NMR (500 MHz, d₃-MeCN, 25°C / ppm): δ = 198.3 (C=O), 197.8 (C=O), 191.8 (C=O), 160.9, 160.7, 158.9, 150.2, 136.1 (CH), 122.4 (CH), 115.2, 114.6 (CH), 23.5 (CH₃), 18.3 (CH₃).

Mass Spectrometry: m/z calcd. [C₁₃H₁₁ClN₃O₃Re₁]+ 477.00; found 476.99

Elemental Analysis (CHN): Calculated for C₁₃H₁₁ClN₃O₃Re: C, 32.60, H, 2.32, N, 8.77 Found C, 32.73, H, 2.35, N, 8.30

IR (DCM / cm⁻¹): 2964, 2933, 2870, 2025, 1916, 1899, 1723, 1291

UV-Visible Absorption Spectrum (DCM): λ_{max} = 338 nm, ϵ = 1.3 x 10⁴ mol ⁻¹ dm⁻³ cm⁻¹

Melting Point: 293-295 °C (decomp.)

Characterisation

Powder x-ray diffraction



Figure S1: Powder X-ray Diffraction pattern of $g-C_3N_4$ and $[ReCl(CO)_3(g-C_3N_4)]$. The peaks marked with (*) are from the aluminium holder.



Scanning electron microscopy

Figure S2: SEM of a) $g-C_3N_4$; b) [ReCl(CO)₃($g-C_3N_4$)].

X-Ray Photoelectron Spectroscopy



Figure S3 XPS Spectra of a) N 1s g-C₃N₄; b) N 1s [ReCl(CO)₃(g-C₃N₄)]; c) Re 4f [ReCl(CO)₃(g-C₃N₄)].

Sample	Region	Peak / eV	FWHM / eV	Assignment
g-C ₃ N ₄	N 1s	398.7	1.14	CNC
		400.0	1.29	NC ₃
		401.1	1.46	CNH
	C 1s	288.2	1.11	C=N
		286.1	1.03	C=O
		284.8	1.07	C-NH

Table S1: XPS	fitted	neaks for	g-C ₂ N
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Sample	Region	Peak / eV	FWHM / eV	Assignment
$[\operatorname{ReCl}(\operatorname{CO})_3(\operatorname{g-C}_3\operatorname{N}_4)]$	N 1s	398.7	1.20	CNC
		400.0	1.29	NC ₃
		401.1	1.46	CNH
	C 1s	292.0	1.50	π-π*
		288.6	1.49	C=N
		286.6	1.50	C=O
		284.8	1.50	C-N
	Re 4f	44.6	1.25	Re (I) 4f _{7/2}
		42.2	1.25	Re (I) 4f _{5/2}

Table S2: XPS fitted peaks for $[ReCl(CO)_3(g-C_3N_4)]$.

ATR-IR



Figure S4: solid state ATR-IR spectra of $g-C_3N_4$ and $[ReCl(CO)_3(g-C_3N_4)]$.

DRIFTS of [ReCl(CO)₃(g-C₃N₄)]



Figure S5: DRIFTS spectra of g-C₃N₄ and [ReCl(CO)₃(g-C₃N₄)].

Leaching study

ATR-IR spectroscopy



Figure S6: ATR Infra-red spectroscopy of $[ReCl(CO)_3(g-C_3N_4)]$ after soaking in different solvents. a) 500-400 cm⁻¹ and b) 1800-2100 cm⁻¹. All spectra were normalised to the g-C₃N₄ peak at 1250 cm⁻¹.



Liquid IR spectroscopy

Figure S7: Liquid infra-red spectroscopy of supernatant after soaking of $[ReCl(CO)_3(g-C_3N_4)]$ in various

solvents.

Solid State ¹³C CP-MAS NMR



Figure S8: The ${}^{13}C$ CP-MAS NMR spectrum (10 kHz spin rate) of [ReCl(CO)₃(g-C₃N₄)] (top) and g-C₃N₄ (bottom).

Scanning Transmission Electron Microscopy



Figure S9: HAADF images of $[ReCl(CO)_3(g-C_3N_4)]$. Image b) is the region inside the red box shown in image a).





Figure S10. Example EDX of two regions of $[ReCl(CO)_3(g-C_3N_4)]$. Red peaks are darker area (red ring) and yellow peaks are brighter area (yellow ring)



Figure S11. HAADF images of $[ReCl(CO)_3(g-C_3N_4)]$ and intensity scanned across a line between the two arrows in the top right image. The HAADF images were smoothed using the smooth spatial filter analysis in Gatan Digital Micrograph software to reduce noise. In comparison the size of a single atom of Pt has been measured (on a carbon film) as 0.11 ± 0.1 nm in diameter on the same instrument.²

Single crystal data for [ReCl(CO)₃(DMNA)]

Parameter	[ReCl(CO) ₃ (DMNA)]
Empirical Formula	C ₁₃ H _{12.18} ClN ₃ O _{3.59} Re
Formula Weight	489.50
Temperature / K	110.05(10)
Crystal System	Monoclinic
Space Group	C _{2/c}
a / Å	12.6764(2)
b / Å	12.05740(10)
c / Å	20.0284(2)
α/°	90
β/°	95.0420(10)
γ/°	90
Volume / ų	3049.38(6)
Z	8
$\rho_{calc} g/cm^3$	2.132
μ / mm-1	8.162
F(000)	1855.0
Crystal Size / mm ³	0.153x0.101x0.017
Radiation	ΜοΚα (λ=0.71073)
2 $ heta$ range for collection / °	7.06-64.176
Index Ranges	-18≥h≥18, -17≥k≥17, -29≥l≥28
Reflections Collected	19729
Independent Reflections	4946 [R _{int} =0.0314, R _{sigma} = 0.0257]
Data/Restraints/Parameters	4946/0/226
Goodness-of-fit on F ²	1.102
Final R indexes [I $\ge 2\sigma$ (I)]	R ₁ =0.0254 wR ₂ =0.0511
Final R indexes [all data]	$R_1=0.0291 \text{ w} R_2=0.0525$
Largest diff. peak/hole /e Å ⁻³	1.52/-2.00

Table S3: Acquisition and refinement data for $[ReCl(CO)_3(DMNA)]$.

Bond Distance / Å	[ReCl(CO) ₃ (DMNA-κ ² <i>N</i> , <i>N</i> ')]
M-N1	2.212(2)
M-N2	2.218(2)
M-C11	1.912(4)
C11-O1	1.149(4)
M-C12	1.896(4)
C12-O2	1.141(4)
M-C13	1.899(3)
C13-O3	1.150(4)
M-Cl1	2.4935(9)
Bond Angle / °	
N1-M-N2	60.41(8)
C11-M-C12	86.4(2)
C12-M-C13	88.6(1)
C13-M-C11	88.4(1)
N1-M-C13	90.9(1)
N1-M-Cl1	85.89(6)
N2-M-C13	96.3(1)
N2-M-Cl1	81.71(6)

Table S4: Selected bond distances for [ReCl(CO)₃(DMNA- $\kappa^2 N$, N')].

Table S5: Bond distance and angles in DMNA showing distortion upon coordination in

[ReCl(CO) ₃ (DMNA-κ ²	Ν,	N′)].
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Bond Distance / Å	DMNA	[ReCl(CO) ₃ (DMNA)]
C1-C8	1.424(3)	1.395(3)
N1-N2	2.304(3)	2.229(3)
N3-C2	1.353(5)	1.341(4)
Bond Angle / °		
Bond Angle / °		
Bond Angle / ° N1-C1-N2	115.6(2)	110.1(2)

References

- S. P. Schmidt, W. C. Trogler, F. Basolo, M. A. Urbancic and J. R. Shapley, *Inorganic Syntheses*, ed. R. J. Angelici, 2007, 28, 161.
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