

Electronic Supplementary Information for

Trans [O=Re^V-OH] Core Stabilised by Chelating N-Heterocyclic Dicarbene Ligands

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1. Experimental Section

Synthesis of Ag(I) NHC complexes and characterisation

$L^{\text{Me}}\text{Br}_2$, $L^{\text{iPr}}\text{Br}_2$, and $L^{\text{Bn}}\text{Br}_2$ were synthesized according to literature procedures¹ with modifications. To a solution of $L^{\text{Me}}\text{Br}_2$, $L^{\text{iPr}}\text{Br}_2$ or $L^{\text{Bn}}\text{Br}_2$ (0.59 mmol) in H_2O (8.0 mL), two equivalent of Ag_2O (1.2 mmol) was added in the absence of light. The reaction was stirred at room temperature for $L^{\text{Me}}\text{Br}_2$ and $L^{\text{iPr}}\text{Br}_2$, and at 50 °C for $L^{\text{Bn}}\text{Br}_2$, and stopped when the mixture turned brown. Excess Ag_2O was filtered and residue washed with H_2O . To the reddish brown filtrate, two equivalent of NH_4PF_6 (1.2 mmol) was added and stirred. White precipitate in colourless solution was formed immediately. White precipitate was collected by filtration. The product was washed with H_2O and Et_2O and dried under vacuum. Light grey complexes $\text{Ag}_2(\text{L}^{\text{Me}})_2(\text{PF}_6)_2$, $\text{Ag}_2(\text{L}^{\text{iPr}})_2(\text{PF}_6)_2$, $\text{Ag}_2(\text{L}^{\text{Bn}})_2(\text{PF}_6)_2$ were obtained.

$\text{Ag}_2(\text{L}^{\text{Me}})_2(\text{PF}_6)_2$. Yield: 57%. ^1H NMR ($\text{DMSO}-d_6$, 300MHz): δ 7.866 and 7.860 (d, 1H, $^3J=1.8\text{Hz}$, $\text{CH}=\text{CH}$), δ 7.532 and 7.526 (d, 1H, $^3J=1.8\text{Hz}$, $\text{CH}=\text{CH}$), δ 6.61 (b, 1H, NCH_2N), δ 3.86 (s, 3H, CH_3). ^{13}C NMR ($\text{DMSO}-d_6$, 300MHz): δ 124.37 ($\text{CH}=\text{CH}$), δ 121.71 ($\text{CH}=\text{CH}$), δ 63.14 (NCH_2N), δ 38.57 (CH_3), imidazole NCN not observed.

$\text{Ag}_2(\text{L}^{\text{iPr}})_2(\text{PF}_6)_2$. Yield: 72%. ^1H NMR ($\text{DMSO}-d_6$, 300MHz): δ 7.88 (s, 2H, $\text{CH}=\text{CH}$), δ 7.74 (s, 2H, $\text{CH}=\text{CH}$), δ 6.55 (b, 2H, NCH_2N), δ 4.61-4.74 (septet, 2H, $^3J=6.54\text{Hz}$, $\text{CH}(\text{CH}_3)_2$), δ 1.44 and 1.42 (d, 12H, $^3J=6.75\text{Hz}$, CH_3). ^{13}C NMR ($\text{DMSO}-d_6$, 300MHz): δ 122.20 ($\text{CH}=\text{CH}$), δ 120.03 ($\text{CH}=\text{CH}$), δ 63.86 (NCH_2N), δ 54.47 ($\text{CH}(\text{CH}_3)_2$), δ 23.35 (CH_3), imidazole NCN not observed.

$\text{Ag}_2(\text{L}^{\text{Bn}})_2(\text{PF}_6)_2$. Yield: 64%. ^1H NMR ($\text{DMSO}-d_6$, 400MHz): δ 7.88 (s, 1H, $\text{CH}=\text{CH}$), δ 7.60 (s, 1H, $\text{CH}=\text{CH}$), δ 7.28- 7.23 (m, 5H, Ph), δ 7.07 (s, 1H, NCH_2N), δ 5.21 (s, 2Hs, NCH_2Ph). ^{13}C NMR ($\text{DMSO}-d_6$, 100MHz): δ 128.99- δ 127.13 (Ph), δ 123.55 ($\text{CH}=\text{CH}$), δ 122.40 ($\text{CH}=\text{CH}$), δ 63.59 (NCH_2N), δ 54.48 (CHPh), imidazole NCN not observed.

Synthesis of complexes 1-3

$\text{Ag}_2\text{L}_2(\text{PF}_6)_2$ (0.05 mmol) ($\text{L} = \text{L}^{\text{Me}}$, L^{iPr} , or L^{Bn}) was added to a CH_3CN solution (10.0 mL) of $\text{ReOCl}_3(\text{PPh}_3)_2$ (0.05 mmol).² The suspension turned from green-yellow to dirty green and then brown in 20 min. The mixture was stirred for 2 h, then AgCl was filtered off. The reddish brown filtrate was evaporated to dryness under reduced pressure. The crude product was washed with toluene, ethyl acetate and Et_2O to yield $[\text{ReO}(\text{OH})(\text{L}^{\text{Me}})_2](\text{PF}_6)(\text{ReO}_4)$ (**1**), $[\text{ReO}(\text{OH})(\text{L}^{\text{iPr}})_2](\text{PF}_6)(\text{ReO}_4)$ (**2**) or $[\text{ReO}(\text{OH})(\text{L}^{\text{Bn}})_2](\text{PF}_6)(\text{ReO}_4)$ (**3**).

$[\text{ReO}(\text{OH})(\text{L}^{\text{Me}})_2](\text{PF}_6)_{1.4}(\text{ReO}_4)_{0.6}$ (**1**): Yield: 92%. ESI-MS: $m/z=286.14$ (100%, $[\text{ReO}(\text{OH})(\text{L}^{\text{Me}})_2]^{2+}$). ^1H NMR ($\text{DMSO}-d_6$, 400MHz): δ 7.93 (s, 2H, $\text{CH}=\text{CH}$), δ 7.92 (s, 2H, $\text{CH}'=\text{CH}$), δ 7.76 (s, 2H, $\text{CH}=\text{CH}$), δ 7.67 (s, 2H, $\text{CH}=\text{CH}'$), δ 6.76 (s, 2H, NCH_2N), δ 6.71 (s, 2H, $\text{NCH}'_2\text{N}$), δ 3.77 (s, 6H, CH_3), δ 3.55 (s, 6H, CH'_3). ^{13}C NMR ($\text{DMSO}-d_6$, 100MHz): δ 168.42 (Re-C), δ 166.68 (Re-C'), δ 125.23 ($\text{CH}=\text{CH}$), δ 124.53 ($\text{C}'\text{H}=\text{CH}$), δ 123.50 ($\text{CH}=\text{CH}$), δ 122.76 ($\text{CH}=\text{C}'\text{H}$),

δ 63.91 (NCH₂N), δ 62.97 (NC'H₂N), δ 37.43 (CH₃), δ 36.55 (C'H₃). FTIR (400-4000cm⁻¹, KBr): 3442cm⁻¹ (OH), 960cm⁻¹ (Re=O), 923cm⁻¹ (ReO₄⁻), 842 and 559cm⁻¹ (PF₆⁻). Analytical calculation for C₁₈H₂₅N₈O_{4.42}P_{1.40}F_{8.38}Re_{1.61}, C: 23.49, H: 2.73, N: 12.17 %. Found, C: 22.27, H: 2.47, N: 11.55 %.

[ReO(OH)(L^{iPr})₂](PF₆)_{1.4}(ReO₄)_{0.6} (2): Yield: 96%. ESI-MS: $m/z = 342.07$ (90%, [ReO(OH)(L^{iPr})₂]²⁺). ¹H NMR (DMSO-d₆, 400MHz): δ 7.94 (s, 2H, CH=CH), δ 7.87 (s, 2H, CH=CH), δ 6.71 (s, 2H, NCH₂N), δ 4.46 (s, 1H, CH(CH₃)₂), δ 4.21 (s, 1H, CH'(CH₃)₂), δ 1.55 and δ 1.49 (d, 6H, CH₃), δ 1.00 and δ 0.97 (d, 6H, CH'₃). ¹³C NMR (DMSO-d₆, 100MHz): δ 167.54 (Re-C), δ 123.75 (CH=CH), δ 118.73 (CH=CH), δ 63.38 (NCH₂N), δ 52.62 (CH(CH₃)₂), δ 51.92 (C'H(CH₃)₂), δ 22.34 (CH₃), δ 21.60 (C'H₃). FTIR (400-4000cm⁻¹, KBr): 3438cm⁻¹ (OH), 963cm⁻¹ (Re=O), 913cm⁻¹ (ReO₄⁻), 842 and 558cm⁻¹ (PF₆⁻). Analytical calculation for C₂₆H₄₁N₈O_{4.37}P_{1.41}F_{8.44}Re_{1.59}, C: 30.15, H: 3.99, N: 10.81 %. Found, C: 30.70, H: 3.83, N: 10.63 %.

[ReO(OH)(L^{Bn})₂](PF₆)_{1.3}(ReO₄)_{0.7} (3): ESI-MS: $m/z = 875.27$ (100%, [ReO₂(L^{Bn})₂]⁺).

X-ray crystallography

Crystallographic measurements were made on a Bruker AXS APEX diffractometer by using graphite-monochromated Mo K α ($\lambda = 0.71073 \text{ \AA}$). The data were corrected for Lorentz and polarization effects with the SMART suite of programs and for absorption effects with SADABS.³ All crystal structures were solved by direct methods and refined on F^2 by full-matrix least-squares techniques with SHELXTL-97 program.⁴ In **1** and **3** the occupancy factors for disordered [PF₆]/[ReO₄] were refined to be 0.70/0.30 and 0.65/0.35 respectively. The H atoms on the OH group were found from difference Fourier map but treated with disordered model with their occupancy factors fixed at 0.50 and O–H bond lengths restrained at 0.85 \AA while allowing their thermal parameters to be refined freely. For complex **2**, the occupancy factors for the two disordered [PF₆]/[ReO₄] pairs were refined to be 0.66/0.34 and 0.75/0.25. The H atom from the OH group were located from difference Fourier map with O–H bond lengths restrained at 0.82 \AA and thermal parameters ($U_{\text{iso(H)}}=1.2U_{\text{eq(O)}}$). All non-hydrogen atoms were refined anisotropically. All other hydrogen atoms were calculated in ideal geometries and refined isotropically. A summary of the key crystallographic data for complexes **1–3** are listed in Table S1 and their selected bond distances and angles are listed in Table S2.

Table S1 Summary of key crystallographic data for complexes **1–3**.

Complex	1	2	3
Empirical formula	C ₂₂ H ₃₁ F _{8.38} N ₁₀ O _{4.42} P _{1.4} Re _{1.61}	C ₂₆ H ₄₁ F _{8.44} N ₈ O _{4.37} P _{1.41} Re _{1.59}	C ₅₀ H ₅₃ F _{7.8} N ₁₂ O _{4.8} P _{1.3} Re _{1.7}
Formula weight	1007.78	1024.92	1378.79
Temperature (K)	223(2)	293(2)	223(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁	<i>P</i> 2 ₁ /n
Unit cell dimensions			
<i>a</i> (Å)	8.3330(5)	9.043(1)	11.6582(6)
<i>b</i> (Å)	9.7967(6)	17.836(2)	11.1157(6)
<i>c</i> (Å)	11.5140(7)	11.784(1)	22.029(1)
α (°)	112.133(1)		
β (°)	97.526(1)	110.328(3)	102.791 (1)
γ (°)	101.004(1)		
Volume (Å ³)	833.13(9)	1782.1(3)	2783.9(3)
<i>Z</i>	1	2	2
Density (calculated, Mg/m ³)	2.008	1.931	1.645
Absorption coefficient (mm ⁻¹)	5.996	5.555	3.815
F(000)	484.8	1001	1385.2
Crystal size (mm ³)	0.50 × 0.24 × 0.20	0.50 × 0.34 × 0.20	0.18 × 0.12 × 0.10
θ range for data collection (°)	1.96–27.50	2.17–24.99	1.83–27.50
Reflections collected	10815	10532	19182
Independent reflections	3821 [<i>R</i> _{int} = 0.0308]	6224 [<i>R</i> _{int} = 0.0275]	6379 [<i>R</i> _{int} = 0.0523]
Data/restraints/parameters	3821 / 66 / 267	6224 / 126 / 515	6379 / 239 / 380
Goodness of fit on F ²	1.243	1.270	1.108
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0386, w <i>R</i> ₂ = 0.0915	<i>R</i> ₁ = 0.0444, w <i>R</i> ₂ = 0.1039	<i>R</i> ₁ = 0.0611, w <i>R</i> ₂ = 0.1285
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0407, w <i>R</i> ₂ = 0.0925	<i>R</i> ₁ = 0.0450, w <i>R</i> ₂ = 0.1042	<i>R</i> ₁ = 0.0827, w <i>R</i> ₂ = 0.1373
Largest diff. peak and hole (e.Å ⁻³)	1.248 and -1.356	1.662 and -1.299	1.759 and -0.981

Table S2 Selected bond distances (Å) and angles (°) for complexes **1–3**.

	1	2	3
Re(1)-O(1)	1.946(4)	1.779(6)	1.813(4)
Re(1)-O(2)		1.831(7)	
Re(1)-C(1)	2.155(5)	2.17(1)	2.166(7)
Re(1)-C(5)	2.154(4)	2.167(9)	
Re(1)-C(14)		2.164(9)	
Re(1)-C(18)		2.19(1)	
Re(1)-C(12)			2.166(7)
O(1)-Re(1)-O(1A)	180.0(2)		180
O(1)-Re(1)-O(2)		179.6(3)	
O(1)-Re(1)-C(1)	87.7(2)	90.5(3)	90.0(2)
O(1)-Re(1)-C(1A)	92.3(2)		90.0(2)
O(1)-Re(1)-C(5)	89.4(2)	90.4(3)	
O(1)-Re(1)-C(5A)	90.6(2)		
O(1)-Re(1)-C(12)			90.7(2)
O(1)-Re(1)-C(12A)			89.3(2)
O(1)-Re(1)-C(14)		91.4(3)	
O(1)-Re(1)-C(18)		89.6(4)	
O(2)-Re(1)-C(1)		89.5(4)	
O(2)-Re(1)-C(5)		89.2(3)	
O(2)-Re(1)-C(14)		89.0(3)	
O(2)-Re(1)-C(18)		90.4(4)	
C(5)-Re(1)-C(1)	81.4(2)	80.1(3)	
C(5)-Re(1)-C(1A)	98.6(2)		
C(5)-Re(1)-C(18)		100.1(3)	
C(14)-Re(1)-C(1)		99.1(4)	
C(14)-Re(1)-C(18)		80.7(4)	
C(1)-Re(1)-C(12)			81.3(2)
C(1)-Re(1)-C(12A)			98.7(2)
C(5A)-Re(1)-C(5)	180		
C(1A)-Re(1)-C(1)	180		180
C(5)-Re(1)-C(14)		178.0(4)	
C(1)-Re(1)-C(18)		179.8(4)	
C(12A)-Re(1)-C(12)			180.0(3)

Symmetry code A for complex **1**, 1-x, 1-y, -z; for complex **3**: -x, 2-y, -z.

References

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