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Electronic Supplementary Information

**Mononuclear rhenium(I) complexes incorporating
2-(Arylazo)phenyl benzyl thioethers: synthesis,
structure, spectral, DFT and TDDFT study**

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IR and NMR spectra

The IR spectra of all the complexes were recorded as a KBr disc. The complexes display three metal carbonyl vibrations in the region 1904–2043 cm^{-1} . These vibrations are consistent with the presence of *fac*- $[\text{Re}(\text{CO})_3]^+$ core in the complex with pseudo C_{3v} symmetry. The N=N stretches are observed $\sim 1455 \text{ cm}^{-1}$. The Re–Cl stretching frequency for all the complexes is observed $\sim 305 \text{ cm}^{-1}$. The frequencies calculated by DFT method using the gas-phase optimized structure predict three carbonyl vibrations with a_1 and e symmetries¹ for all the complexes. The experimental and calculated IR spectral data are given in Experimental section.

The complexes are diamagnetic and display well resolved ^1H and ^{13}C NMR spectra in CDCl_3 solution at room temperature. The assignment of NMR spectra is based on intensity and spin-spin splitting structure of Re(I) complexes.

In all the complexes the C(18)–H proton is observed as a doublet $\sim 7.8 \text{ ppm}$. The aromatic protons span in the range (6.95–7.94) ppm. The resonance of CH_2 group attached to the coordinated sulfur atom is observed as singlet $\sim 4.25 \text{ ppm}$.

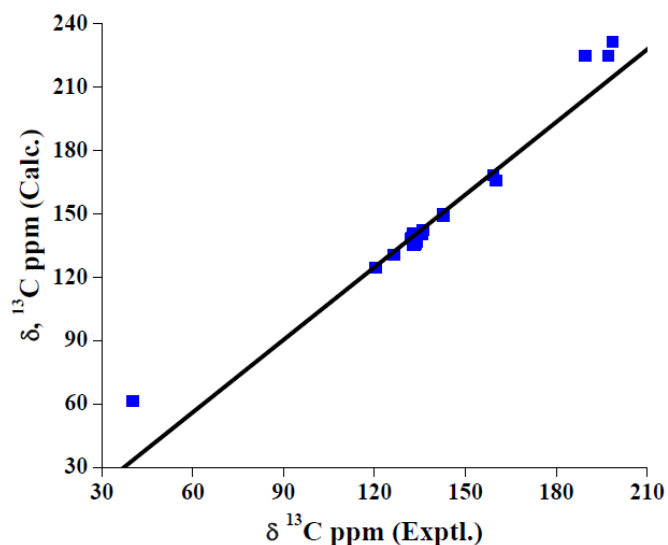


Fig. S1 Linear correlation between the experimental and calculated ^{13}C NMR chemical shifts of $[\text{Re}(\text{L}^1)(\text{CO})_3\text{Cl}]$, **1**.

The complexes show three metal carbonyl resonances in the region 189–199 ppm which corroborates with the presence of pseudo C_{3v} *fac*- $[\text{Re}(\text{CO})_3]^+$ core.² The closely spaced

resonances (~ 199 and ~ 198 ppm) are assigned as equatorial carbonyls whereas the resonance ~ 190 ppm is due to the axial carbonyl group. The differences in chemical shift values can be attributed to different π accepting property of azo nitrogen, chlorine and sulfur atom. The ^1H and ^{13}C NMR spectral chemical shifts were calculated by GIAO-DFT method and the calculated chemical shifts are in good agreement with the experimental data. The correlation between the experimental and calculated ^{13}C NMR chemical shift of complex **1** is shown in Fig. S1. The experimental and calculated ^1H and ^{13}C NMR data are given in the Experimental section.

Table S1 Energies (eV) and composition (%) of frontier molecular orbitals of the complex $[\text{Re}(\text{L}^2)(\text{CO})_3\text{Cl}]$, **2** at ground state (S_0)

Orbital	Energy (eV)	Contribution (%)				Main bond type
		Re	CO	L^2	Cl	
LUMO + 5	-1.011	1.0	23.5	74.1	1.4	$\pi^*(\text{CO}) + \pi^*(\text{L}^2)$
LUMO + 4	-1.098	4.1	6.4	88.0	1.5	$\pi^*(\text{L}^2)$
LUMO + 3	-1.483	8.9	28.9	61.7	0.5	$\pi^*(\text{CO}) + \pi^*(\text{L}^2)$
LUMO + 2	-1.674	23.7	55.5	20.3	0.5	$\text{p}(\text{Re}) + \pi^*(\text{CO}) + \pi^*(\text{L}^2)$
LUMO + 1	-1.779	22.1	35.6	40.0	2.2	$\text{p}(\text{Re}) + \pi^*(\text{CO}) + \pi^*(\text{L}^2)$
LUMO	-3.591	1.3	2.9	94.1	1.6	$\pi^*(\text{L}^2)$
HOMO	-6.654	33.1	15.8	28.1	23.0	$\text{d}(\text{Re}) + \pi(\text{CO}) + \pi(\text{L}^2) + \text{p}(\text{Cl})$
HOMO - 1	-6.770	42.7	19.6	10.9	26.8	$\text{d}(\text{Re}) + \pi(\text{CO}) + \pi(\text{L}^2) + \text{p}(\text{Cl})$
HOMO - 2	-7.096	21.2	9.6	55.2	14.0	$\text{d}(\text{Re}) + \pi(\text{L}^2) + \text{p}(\text{Cl})$
HOMO - 3	-7.176	10.5	2.5	73.7	13.3	$\text{d}(\text{Re}) + \pi(\text{L}^2) + \text{p}(\text{Cl})$
HOMO - 4	-7.217	45.0	19.7	34.0	1.3	$\text{d}(\text{Re}) + \pi(\text{CO}) + \pi(\text{L}^2)$
HOMO - 5	-7.313	0.9	0.4	98.4	0.3	$\pi(\text{L}^2)$

Table S2 Energies (eV) and composition (%) of frontier molecular orbitals of the complex [Re(L³)(CO)₃Cl], **3** at ground state (S₀)

Orbital	Energy (eV)	Contribution (%)				Main bond type
		Re	CO	L ³	Cl	
LUMO + 5	-1.280	2.4	10.8	86.5	0.2	$\pi^*(\text{CO}) + \pi^*(\text{L}^3)$
LUMO + 4	-1.535	9.0	28.8	61.8	0.4	$\pi^*(\text{CO}) + \pi^*(\text{L}^3)$
LUMO + 3	-1.705	23.1	56.5	20.3	0.1	$p(\text{Re}) + \pi^*(\text{CO}) + \pi^*(\text{L}^3)$
LUMO + 2	-1.841	20.9	33.5	43.4	2.2	$p(\text{Re}) + \pi^*(\text{CO}) + \pi^*(\text{L}^3)$
LUMO + 1	-3.406	1.4	1.9	96.3	0.4	$\pi^*(\text{L}^3)$
LUMO	-4.005	1.1	2.3	96.2	0.4	$\pi^*(\text{L}^3)$
HOMO	-6.794	44.1	20.2	7.6	28.1	$d(\text{Re}) + \pi(\text{CO}) + p(\text{Cl})$
HOMO - 1	-6.853	40.7	18.5	11.0	29.7	$d(\text{Re}) + \pi(\text{CO}) + \pi(\text{L}^3) + p(\text{Cl})$
HOMO - 2	-7.172	7.6	2.9	83.3	6.1	$\pi(\text{L}^3)$
HOMO - 3	-7.279	44.4	20.0	34.6	1.0	$d(\text{Re}) + \pi(\text{CO}) + \pi(\text{L}^3)$
HOMO - 4	-7.331	9.1	4.0	86.9	0.0	$\pi(\text{L}^3)$
HOMO - 5	-7.566	9.0	1.1	86.9	3.0	$\pi(\text{L}^3)$

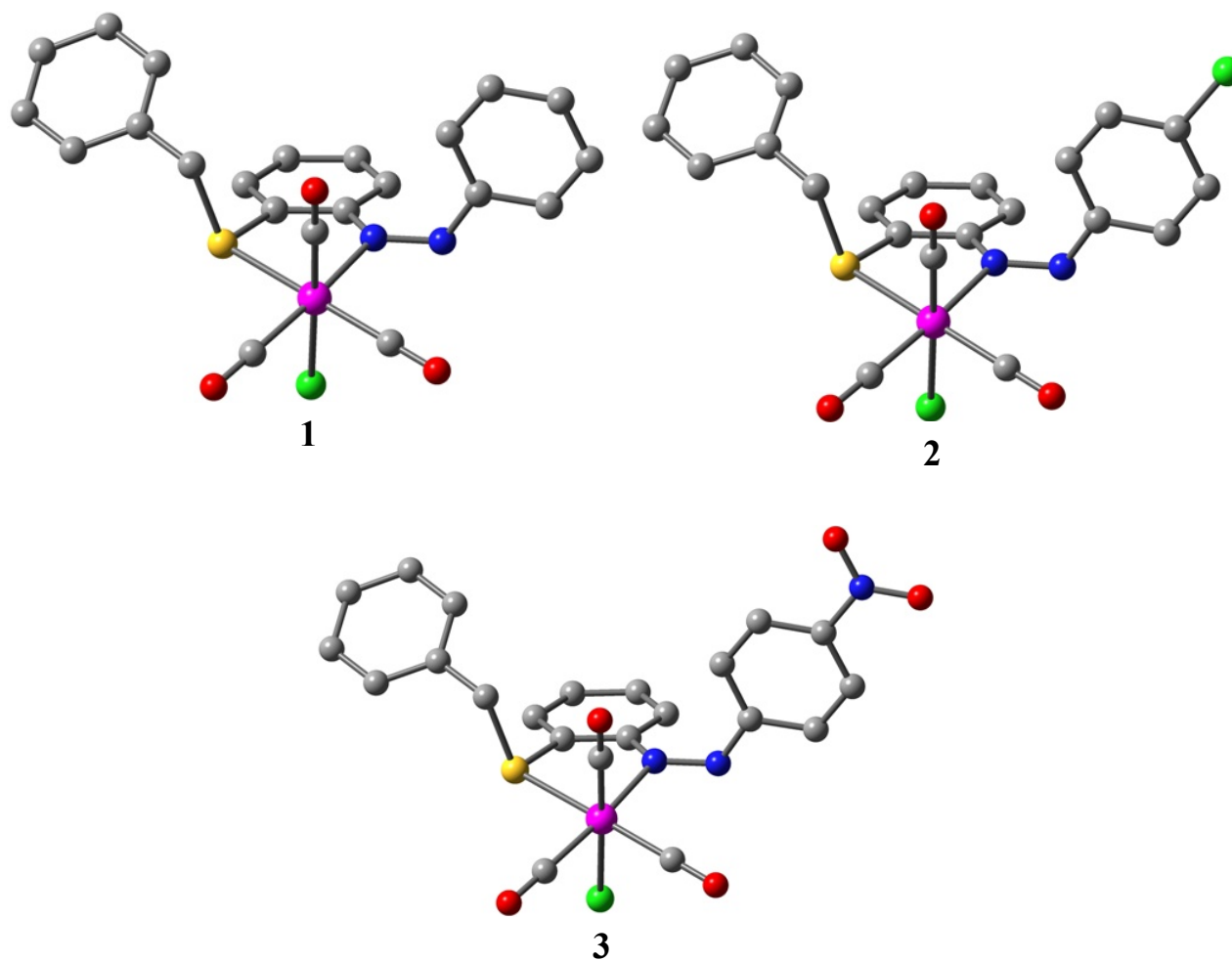


Fig. S2 Optimized molecular structure of $[\text{Re}(\text{L}^1)(\text{CO})_3\text{Cl}]$, **1**; $[\text{Re}(\text{L}^2)(\text{CO})_3\text{Cl}]$, **2** and $[\text{Re}(\text{L}^3)(\text{CO})_3\text{Cl}]$, **3** at lowest lying triplet excited state (T_1) (Re: Pink, Cl: Green, N: Blue, O: Red, S: Yellow, C: Grey). Hydrogen atoms are omitted for clarity.

Table S3 Main calculated optical transition for complex $[\text{Re}(\text{L}^2)(\text{CO})_3\text{Cl}]$, **2** with composition in terms of molecular orbital contribution of the transition, vertical excitation energies and oscillator strength in dichloromethane

Electronic Transitions	Composition	Excitation energy	Oscillator strength (f)	CI ^a	Assign	λ_{exp} (nm)
$S_0 \rightarrow S_4$	HOMO – 4 \rightarrow LUMO	2.9236 eV (424 nm)	0.0846	0.50844	MLCT/ILCT	416
	HOMO – 3 \rightarrow LUMO			–0.41666	MLCT/ILCT	
	HOMO – 2 \rightarrow LUMO			–0.22208	MLCT/ILCT	
$S_0 \rightarrow S_{10}$	HOMO – 9 \rightarrow LUMO	3.7121 eV (334 nm)	0.0550	0.57855	MLCT/ILCT	314
	HOMO – 8 \rightarrow LUMO			0.16174	ILCT	
	HOMO – 7 \rightarrow LUMO			–0.29772	ILCT	
	HOMO – 6 \rightarrow LUMO			0.12068	ILCT	
$S_0 \rightarrow S_{34}$	HOMO – 4 \rightarrow LUMO + 2	5.1000 eV (243 nm)	0.0565	0.12325	MLCT/ILCT	237
	HOMO – 3 \rightarrow LUMO + 2			0.11064	MLCT/ILCT	
	HOMO – 2 \rightarrow LUMO + 2			0.25157	MLCT/ILCT	
	HOMO – 1 \rightarrow LUMO + 5			–0.21136	MLCT/ILCT	

^aCoefficient of the wave function for each excitations. The CI coefficients are in absolute values.

Table S4 Main calculated optical transition for complex $[\text{Re}(\text{L}^3)(\text{CO})_3\text{Cl}]$, **3** with composition in terms of molecular orbital contribution of the transition, vertical excitation energies and oscillator strength in dichloromethane

Electronic Transitions	Composition	Excitation energy	Oscillator strength (f)	CI ^a	Assign	λ_{exp} (nm)
$S_0 \rightarrow S_2$	HOMO – 1 \rightarrow LUMO	2.2253 eV (557 nm)	0.0598	0.65235	MLCT/ILCT	535
	HOMO \rightarrow LUMO			0.20881	MLCT/ILCT	
$S_0 \rightarrow S_{19}$	HOMO – 3 \rightarrow LUMO + 3	3.9725 eV (312 nm)	0.0094	0.10961	MLCT/ILCT	307
	HOMO – 1 \rightarrow LUMO + 3			–0.12324	MLCT/ILCT	
	HOMO \rightarrow LUMO + 2			0.60149	MLCT/ILCT	
	HOMO \rightarrow LUMO + 4			0.26046	MLCT/ILCT	
$S_0 \rightarrow S_{38}$	HOMO – 3 \rightarrow LUMO + 2	4.8449 eV (256 nm)	0.0947	–0.30755	MLCT/ILCT	261
	HOMO – 2 \rightarrow LUMO + 2			0.57849	LMCT/ILCT	
	HOMO – 2 \rightarrow LUMO + 4			–0.12810	ILCT	

^aCoefficient of the wave function for each excitations. The CI coefficients are in absolute values.

References

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- 2 F. Cloran, I. Carmichael and A. S. Serianni, *J. Am. Chem. Soc.*, 2001, **123**, 4781-4791.