



One-pot synthesis of sulphur bridged dinuclear rhenium metallacycles via addition of S–S bond across Re–Re bond

A. Vanitha^a, P. Sathiya^a, S. Sangilipandi^a, Shaikh M. Mobin^b, Bala. Manimaran^{a,*}

^aDepartment of Chemistry, Pondicherry University, Puducherry 605 014, India

^bNational Single Crystal X-ray Diffraction Facility, Indian Institute of Technology-Bombay, Powai, Mumbai 400 076, India

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ABSTRACT

Oxidative addition of diaryl disulphides RSSR to low-valent transition metal carbonyl $\text{Re}_2(\text{CO})_{10}$ with monodentate pyridine ligands bring forth novel sulphur bridged neutral dinuclear rhenium metallacycles $[\text{L}(\text{CO})_3\text{Re}(\mu\text{-SR})_2\text{Re}(\text{CO})_3\text{L}]$ (**1–9**) (L = pyridine ligand, R = aryl group) under one pot reaction conditions. The Metallacycles **1–9** have been characterised by elemental analysis, NMR and IR and absorption spectral analysis. Molecular structures of **4**, **8** and **9** were determined by crystallographic analysis and the structural studies reveal that pyridyl groups attached to metal centres exhibit *cis* conformation.

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1. Introduction

Transition metal complexes containing the disulphide ligand exhibit a wide range of interesting reactivity and chelating ability at the sulphur atoms [1–8]. Metal sulphides are of interest due to their wide application in various platforms, such as, catalyst for the removal of organosulphur compounds from the feedstock [9,10], as solid state lubricant [11], as good electrical conductor [12–15] and for their role in NO storage and transport *in vivo* to stabilize therapeutic protein structures in the biological processes [16–18]. Recent studies have shown that metal disulphides can also exhibit a variety of important nanostructures [19,20] and metal sulphide nanoparticles serve as catalysts with very high reactivities [21–23]. Earlier, sulphur bridged Re and Mn dinuclear complexes $[\text{Re}(\text{CO})_4(\text{SPh})_2]$ were obtained from benzene thiol and metal hydrido complexes [24]. A decade ago, hydrido sulphide bridged dirhenium complexes $[\text{Re}_2(\mu\text{-H})(\mu\text{-SR})(\text{CO})_8]$ [R = H, *n*-Bu, Ph, 2-naphthyl] were generated from $[\text{Re}_2(\text{CO})_8(\text{MeCN})_2]$ precursor with thiols [25]. Rosenberg and coworkers have reported that dimetallic rhenium and manganese complexes $\text{M}_2(\text{CO})_6(\mu\text{-}\eta^4\text{-SC}_6\text{H}_4\text{S}-\text{SC}_6\text{H}_4\text{S})_2$ [M = Re, Mn] were obtained from thiols and metal carbonyls [26], and $[\text{Re}_2(\text{CO})_8(\text{SPh})_2]$

complexes were prepared from the reaction of benzene thiol with $\text{Re}(\text{CO})_5\text{OTf}$ as well as from the reaction of S_2Ph_2 with $\text{Re}_2(\text{CO})_{10}$ under photolytic condition [27,28]. Hetero-multiple bridged rhenium compounds $\text{Re}_2\text{X}_2(\text{CO})_6\text{S}_2\text{Ph}_2$ (X = Br, I) were synthesised from rhenium pentacarbonyl halides and S_2Ph_2 [29,30] where, cleavage of disulphide bond was not observed. Recent literature evinced that $\text{Re}_2(\mu\text{-SPh})_3\text{Cl}_4(\text{PEt}_2\text{Ph}_2)$ was obtained from $\text{Re}_2\text{Cl}_4(\text{PEt}_2\text{Ph})_4$ and Ph_2S_2 [31], anionic $[(\text{CO})_3\text{Mn}(\mu\text{-SC}_8\text{N}_2\text{H}_4\text{o-S-})_2]^{2-}$ complex was prepared from 2,3-quinoxalinedithiol and $[\text{Mn}(\text{CO})_5]^-$ and neutral $[(\text{Mn}(\text{CO})_3)_2(\mu\text{-SC}_6\text{H}_4\text{o-S-S-C}_6\text{H}_4\text{o-}\mu\text{-S-})]$ and $[(\text{Mn}(\text{CO})_3(\mu\text{-SC}_6\text{H}_4\text{o-NH}_2\text{-})_2]$ complexes were synthesised by multi-step processes [32]. Deeming and coworkers have reported that the reaction of $\text{Re}_2(\text{CO})_{10}$ with pyridine-2-thione yielded $[\text{Re}_2(\text{pyS})_2(\text{CO})_8]$ [33] and similar kind of Re and Mn complexes $[\text{M}_2(\mu\text{-pyS})_2(\text{CO})_8]$ were obtained from $[\text{Re}_3(\mu\text{-H})_3(\text{CO})_{11}(\text{MeCN})]$ and $\text{Mn}_2(\text{CO})_{10}$ respectively, with pyridine-2-thiolato ligands [34,35]. The reaction of $\text{Re}(\text{CO})_5\text{Cl}$ with 8-thiohydroxyquinoline hydrochloride afforded the dimeric compound $\text{Re}_2(\text{CO})_6(\text{SX})_2$ [36]. Reactions of diaryl disulphide with $\text{Re}_2(\text{CO})_{10}$ led to the formation of $[\text{Re}_2(\text{CO})_8(\mu\text{-SR})_2]$ in much low yields under thermolytic condition, while similar reactions carried out in presence of pyridyl ligands resulted into the facile formation of $[\text{Re}_2(\text{CO})_6(\text{L})_2(\mu\text{-SR})_2]$ compounds. Herein, we report on the one-pot synthesis of sulphur bridged neutral dinuclear rhenium metallacycles $[\text{L}(\text{CO})_3\text{Re}(\mu\text{-SR})_2\text{Re}(\text{CO})_3\text{L}]$ (**1–9**) via oxidative addition of S–S bond across Re–Re bond by the reaction of $\text{Re}_2(\text{CO})_{10}$ and diaryl disulphides with monodentate pyridine ligands.

* Corresponding author. Tel.: +91 413 2654414; fax: +91 413 2655987.
E-mail address: manimaran.che@pondiuni.edu.in (B. Manimaran).

2. Results and discussion

2.1. Synthesis of sulphur bridged metallacycles **1–9** from Rhenium carbonyl, diaryl disulphides and monodentate pyridine ligands

Synthesis of sulphur bridged Re(I) metallacycles proceeded with simultaneous incorporation of two aryl sulphido ligands to the equatorial sites of *fac*-Re(CO)₃ core with substitution of CO groups by rigid monotopic N-donor ligands to the axial site [37–39]. The formation of metallacycles **1–9** were accomplished by oxidative addition of diaryl disulphide (RSSR) to the rudimentary rhenium carbonyl with monodentate pyridine ligands like pyridine (py), 4-picoline (pic) and 4-phenylpyridine (Phpy) in mesitylene medium (Scheme 1). The formal oxidative cleavage of S–S bond and addition across the rhenium–rhenium bond afforded the sulphur bridged dinuclear neutral metallacycles *cis*-[L(CO)₃Re(μ-SR)₂Re(CO)₃L] (**1–9**) (L = pyridine ligand, R = aryl group). In case of compound **5**, the *trans* isomer has also been obtained as a minor product. Metallacycles **1–9** were soluble in common organic solvents and stable at room temperature.

2.2. Spectroscopic characterisation of compounds **1–9**

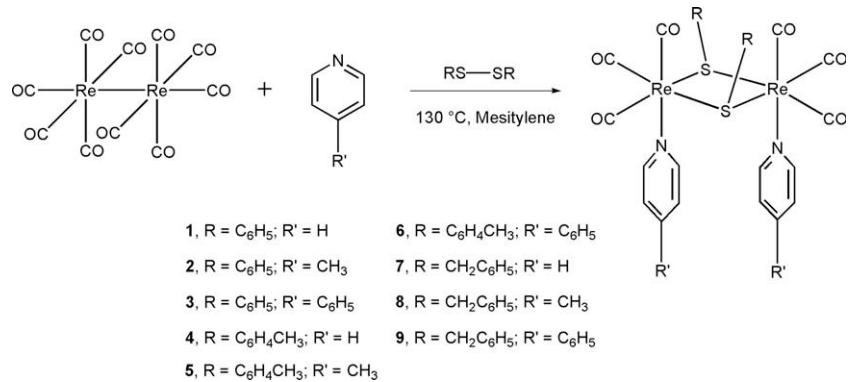
The IR spectrum of compounds **1–9** in CH₂Cl₂ exhibited carbonyl stretching at the region of 2021–1900 cm^{−1} characteristic of facial assembly of three terminal carbonyl ligands (*fac*-Re(CO)₃) in an octahedrally coordinated metal centre [40]. ¹H NMR spectra of compounds **1–9** displayed appropriate signals for the pyridine ligands and aryl groups bonded to bridging sulphur and the data of the compounds were given in experimental section. In ¹H NMR spectra of compounds **1**, **4** and **7** displayed, one doublet, two triplets for pyridyl group (py) protons and phenyl group protons showed one doublet and two triplets. When compared with free pyridine ligand (8.60, 7.65 and 7.26 ppm) and free diaryl disulphide (7.49, 7.30 and 7.23), the pyridyl and aryl group proton signals were shifted towards downfield in compounds. ¹³C NMR of compounds **1**, **4** and **7** showed signals for terminal carbonyl groups at around δ 201–182 ppm with 1:2 ratio and the signals at δ 155–124 ppm were attributed to pyridyl group and the phenyl group carbons resonated at δ 139–126 ppm. The ¹H NMR spectra of compounds **2**, **5** and **8** displayed, two doublets for pyridyl protons and methyl group protons showed a singlet. When compared to uncoordinated ligand, the protons signals were shifted towards the downfield. ¹³C NMR of compounds **2**, **5** and **8** displayed carbonyl group peaks at around δ 201–195 ppm with 1:2 ratio and the signals at δ 155–125 ppm were assigned to pyridyl group and phenyl group carbons appeared at around δ 149–126 ppm. In ¹H NMR spectra of compounds **3**, **6** and **9** displayed, two doublets, one triplet

let and multiplet for phenylpyridine protons and the benzyl group protons showed one doublet, one singlet and multiplet. When compared with free ligand, proton signals of metallacycles were shifted towards upfield except one doublet of pyridyl group. ¹³C NMR of compounds **3**, **6** and **9** exhibited carbonyl group peaks at around δ 200–194 ppm with 1:2 ratio and the signals at δ 156–122 ppm were assigned for pyridyl carbons and signals at around δ 142–126 ppm were assigned to phenyl carbons. The proton signals of benzyl sulphido bridged metallacycles **7–9** were found to be shifted more towards downfield compared to phenyl and p-tolyl sulphido bridged metallacycles **1–3** and **4–6** respectively. Absorption spectra of **1–9** in dichloromethane displayed higher energy transitions at around λ_{max} 226–269 nm, and were attributed to ligand based π – π^* transitions. In addition, phenylpyridine containing compounds **3**, **6** and **9** showed lower energy bands at around λ_{max} 340–358 nm due to MLCT transitions [38,41–48]. Metallacycles **1–9** upon excitation at their respective ligand centred transitions exhibited moderate emissions observed at around 400 nm. However compound **5** showed two emission bands at 280 and 304 nm due to π – π^* excited state of the ligands [49,50].

2.3. Structural characterisation of **4**, **8** and **9**

Single crystals of compounds **4**, **8** and **9** were obtained by slow diffusion of hexane into concentrated solution of compounds in dichloromethane. Crystals of **4** and **8** were obtained at room temperature and for compound **9** crystals were obtained at 5 °C. A good quality single crystals of **4**, **8** and **9** were subjected to X-ray diffraction studies. Details about data collection, solution and refinement were summarized in Table 1 and the molecular structures of compounds **4**, **8** and **9** were depicted in Figs. 1–3, respectively.

Crystal structure of **4** adopted dinuclear metallacyclic structure, where each rhenium in *fac*-Re(CO)₃ core is bonded to one pyridyl and two aryl sulphido group and hence Re centres attained a distorted octahedral geometry with C_{2v} symmetry [33,34,40]. The Re₂S₂ ring is non-coplanar with a dihedral angle of 5.2° between the Re(1)–S(1)–Re(2) and Re(1)–S(2)–Re(2) planes. The Re–Re distance in Re₂S₂ ring is 3.830 Å. The octahedral geometry is associated with the angles of 84.7(1)° for S(1)–Re(1)–N(1), 84.3(1)° for S(2)–Re(1)–N(2), 79.85(4)° for S(1)–Re(1)–S(2) and S(1)–Re(2)–S(2). The two pyridyl groups are oriented in a *cis* conformation and stabilised by weak face-face π – π stacking interaction with a distance of 3.818 Å at C⁴ and C^{4'} carbons of two pyridyl groups (Fig. 1) [51–54]. The two p-tolyl groups bonded to bridging sulphur are arranged in nearly the same plane that of two pyridyl groups and bent away from the Re₂S₂ ring and pyridyl groups. C–H– π interactions were observed in between the two p-tolyl groups of adjacent molecules (2.896 Å) [38,55–58]. C–H–O hydrogen



Scheme 1. Synthesis of sulphur bridged dinuclear metallacycles **1–9**.

Table 1Crystallographic data and structure refinement of **4**, **8** and **9**.

Compound	4	8	9
Empirical Formula	C ₃₀ H ₂₄ N ₂ O ₆ Re ₂ S ₂	C ₃₂ H ₂₈ N ₂ O ₆ Re ₂ S ₂	C ₄₂ H ₃₂ N ₂ O ₆ Re ₂ S ₂
Formula weight	945.03	973.08	1097.22
Crystal system	Tetragonal	Monoclinic	Monoclinic
T (K)	150(2)	293(2) K	150(2)
Space group	P 41 21 2	p 21/n	p 21/n
<i>a</i> (Å)	10.3069(3)	14.3664(5)	9.8062(8)
<i>b</i> (Å)	10.3069(3)	15.1547(6)	17.0820(11)
<i>c</i> (Å)	28.9013(14)	15.8619(8)	23.360(2)
α (°)	90	90	90
β (°)	90	103.271(4)	99.369(8)
γ (°)	90	90	90
<i>V</i> (Å ³)	3070.2(2)	3361.2(2)	3860.8(5)
<i>Z</i>	4	4	4
<i>F</i> (0 0 0)	1792	1856	2112
<i>D</i> _{calc} (mg m ⁻³)	2.044	1.923	1.888
μ (mm ⁻¹)	8.059	7.364	6.424
<i>h</i> , <i>k</i> , <i>l</i> collected	-12,12; -12,10; -34, 34	-12,17; -16,18; -18,18	-11,11; -20, 20; -27, 27
Theta range for data collection (°)	3.13–25.00	2.99–25.00	3.33–25.00
Crystal size (mm)	0.32 × 0.28 × 0.25	0.38 × 0.32 × 0.28	0.23 × 0.18 × 0.15
Reflections collected/unique	24 479/2710	13 222/5703	28 289/6784
<i>R</i> _{int}	0.0969	0.0386	0.0894
Data/restraints/parameters	2710/0/191	5703/0/399	6784/0/487
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0294, <i>wR</i> ₂ = 0.0420	<i>R</i> ₁ = 0.0404, <i>wR</i> ₂ = 0.0840	<i>R</i> ₁ = 0.0542, <i>wR</i> ₂ = 0.1391
Goodness-of-fit (GOF) on <i>F</i> ²	1.168	1.029	1.096
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0307, <i>wR</i> ₂ = 0.0423	<i>R</i> ₁ = 0.0736, <i>wR</i> ₂ = 0.0944	<i>R</i> ₁ = 0.0680, <i>wR</i> ₂ = 0.1439
Largest difference in peak and hole (e Å ⁻³)	0.539 and -0.658	1.291 and -0.742	4.172 and -1.584

bondings were viewed in between C³ of *p*-tolyl moiety and carbonyl group with a distance of 2.701 Å, and H² proton of pyridyl group bonding with another carbonyl group with a distance of 2.597 Å [59–61].

Crystal structure of **8** adopted a dinuclear metallacyclic structure, where each rhenium in *fac*-Re(CO)₃ core is bonded to one picoline and two benzyl sulphido group and hence Re centres attained a distorted octahedral geometry. The Re₂S₂ ring is non-coplanar with a dihedral angle of 7.74° between the Re(1)-S(1)-Re(2) and Re(1)-S(2)-Re(2) planes. The Re-Re distance in Re₂S₂ ring is 3.837 Å. The octahedral geometry is associated with the angles of 84.1(2)° for N(1)-Re(1)-S(1), 85.6(2)° for N(2)-Re(2)-S(1), 99.36(8)° for Re(1)-S(1)-Re(2) and 99.64(7)° for Re(2)-S(2)-Re(1). The two pyridyl groups are oriented in a *cis* conformation and stabilised by weak face–face π–π stacking interaction with a distance of 3.809 Å at C⁴ and C⁴' carbons of pyridyl groups (Fig. 2). The two benzyl groups bonded to bridging sulphur are arranged in a same direction and bent away from the Re₂S₂ ring and pyridyl groups. C–H···π interactions were observed among CH₂ group of benzyl and C³ carbon of picoline groups with a distance of 2.879 Å. C–H···O hydrogen bondings were observed in between carbonyl group and C³ carbon of benzyl group (2.696 Å) and C² carbon of picoline group with another carbonyl group (2.495 Å).

Molecular structure of **9** adopted dinuclear metallacyclic structure, where each rhenium in *fac*-Re(CO)₃ core is bonded to one phenylpyridine and two aryl sulphido group and hence Re centres attained a distorted octahedral geometry. The Re(1)-S(1) and

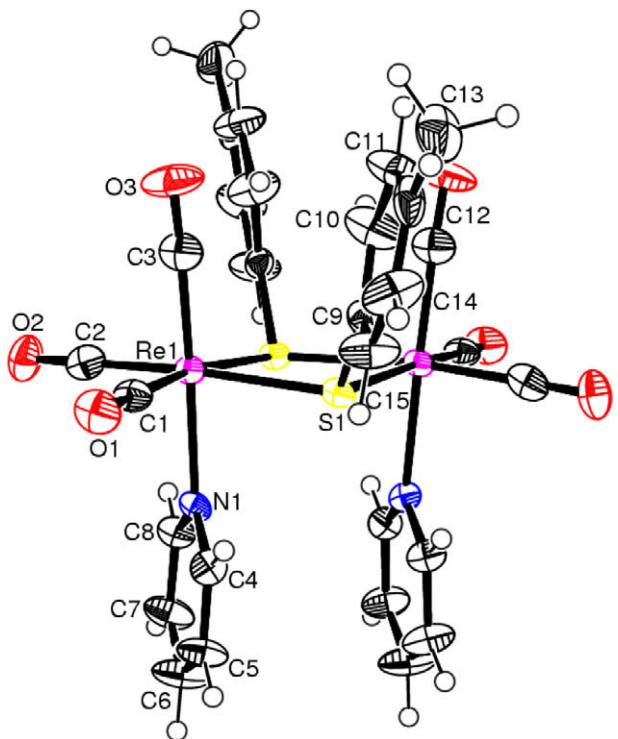


Fig. 1. Molecular structure of **4**. The thermal ellipsoids are drawn at the 50% probability level. Important bond lengths (Å) and angles (°): Re(1)-S(1) 2.492(1), Re(1)-N(1) 2.206(4), Re(1)-S(1)-Re(1) 99.92(4), S(1)-Re(1)-S(1) 79.85(4), N(1)-Re(1)-S(1) 84.7(1).

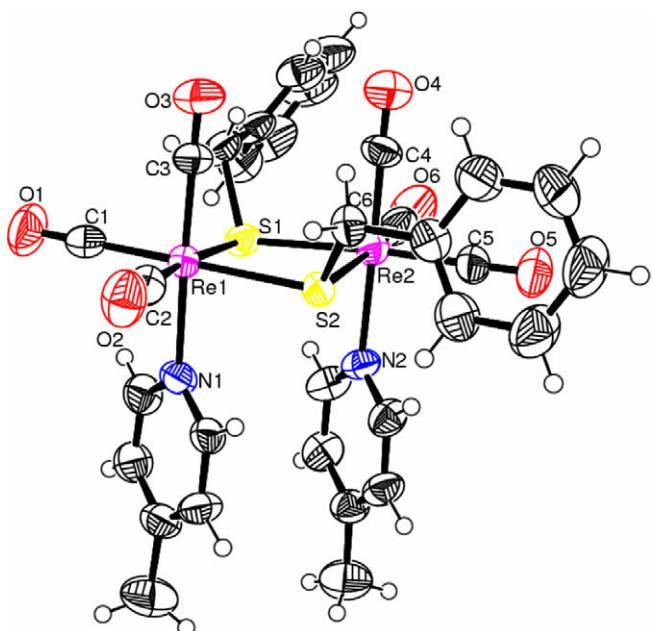


Fig. 2. Molecular structure of **8**. The thermal ellipsoids are drawn at the 50% probability level. Important bond lengths (Å) and angles (°): Re(1)-S(1) 2.510(2), Re(1)-S(2) 2.512(2), Re(2)-S(2) 2.510(2), Re(2)-S(1) 2.523(2), Re(1)-S(1)-Re(2) 99.36(8), Re(2)-S(2)-Re(1) 99.64(7), S(1)-Re(1)-S(2) 80.09(7), S(2)-Re(2)-S(1) 79.88(7).

Re(1)-S(2) distances are not equal and Re₂S₂ ring is non-coplanar with a dihedral angle of 17.85° between Re(1)-S(1)-Re(2) and Re(1)-S(2)-Re(2) planes. In case of molecular structure of **4** and

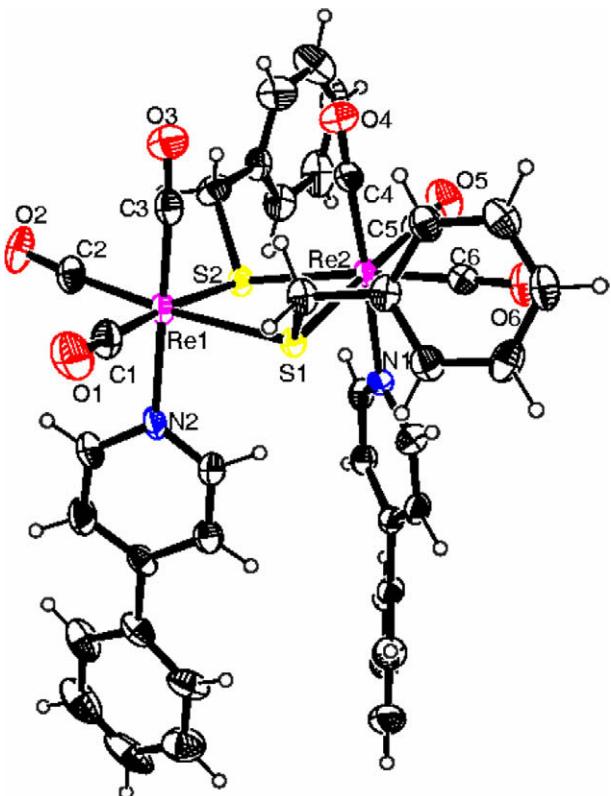


Fig. 3. Molecular structure of **9**. The thermal ellipsoids are drawn at the 30% probability level. Important bond lengths (Å) and angles (°): Re(1)–S(1) 2.517(2), Re(1)–S(2) 2.495(3), Re(2)–S(2) 2.516(2), Re(2)–S(1) 2.516(2), Re(2)–S(1)–Re(1) 98.51(9), Re(1)–S(2)–Re(2) 99.12(9), S(2)–Re(1)–S(1) 78.59(8), S(2)–Re(2)–S(1) 78.22(8).

8 the dihedral angles were found to be 5.2° and 7.74° respectively. The Re–Re distance 3.814 Å in Re_2S_2 ring was found to be decreased whereas $\text{C}^4\text{–C}^4$ distance 4.743 Å was observed to be increased when compared with compounds **4** and **8**. The Re_2S_2 ring was bent towards away from the phenylpyridine ligands. The octahedral geometry was associated with an intraligand angle of 84.7(1)° for S(1)–Re(1)–N(1), 84.3(1)° for S(2)–Re(1)–N(2), 78.58° for S(1)–Re(1)–S(2) and 78.23° for S(1)–Re(2)–S(2). The two phenylpyridine ligands are oriented in a *cis* conformation with a distance of 4.743 Å at $\text{C}^4\text{–C}^4$ carbons of two pyridyl groups (Fig. 3). The phenyl group at para position of the pyridyl ring bonded to Re(1) was twisted by an angle of 99.97°, whereas the other phenyl group of phenylpyridine bonded to Re(2) was twisted by an angle of 121.28°. Two benzyl sulphido groups were bent away from the Re_2S_2 ring. Intermolecular C–H...π interactions were observed in between the phenyl groups of adjacent phenylpyridine ligands (2.856 Å) and in between phenyl group of one phenylpyridine and pyridyl group of another phenylpyridine ligands (2.896 Å). Two benzyl groups were interacted by C–H...π interaction with a distance of 2.880 Å. C–H...O hydrogen bondings were connected the carbonyl group and C^3 of benzyl group with a distance of 2.686 Å and another carbonyl group was interlinked by hydrogen bonding with one benzyl and one phenylpyridine groups (2.558 Å).

3. Experimental

3.1. Instruments and materials

All the reactions were carried out under dry, oxygen-free N_2 atmosphere using standard Schlenk techniques. The starting mate-

rials were purchased from Sigma–Aldrich Chemicals. Rhenium carbonyl, diphenyl disulphide, *p*-tolyl disulphide, dibenzyl disulphide, 4-phenylpyridine were used as received. Pyridine, 4-picoline, mesitylene and other solvents were dried using literature procedure prior to use. IR spectra were taken on a Thermo Nicolet 6700 FT-IR spectrometer. ^1H and ^{13}C NMR were recorded on a Avans Bruker 400 MHz spectrometer. Absorption spectra were recorded on a Varian Cary 5000 UV–Vis spectrophotometer. Emission spectra were recorded on a Fluorolog Horiba jobin Yuvon SPEX-F311 spectrometer. Elemental analysis were performed using Elementar Micro Cube CHN analyzer.

3.2. Synthesis of *cis*–[$\text{L}(\text{CO})_3\text{Re}(\mu\text{-SR})_2\text{Re}(\text{CO})_3\text{L}$], general procedure

A mixture of $\text{Re}_2(\text{CO})_{10}$ (0.3 mmol) and diaryl disulphide (0.2 mmol) were taken in a 50 ml two neck Schlenk flask and fitted with a reflux condenser. The system was evacuated and N_2 was purged. Monodentate pyridine ligand and 30 ml of mesitylene was added in N_2 atmosphere. The reaction mixture was heated to reflux under N_2 for 10–19 h and allowed to cool to room temperature. The mesitylene was removed by vacuum distillation and the solid mixture was washed with hexane, chromatographed on silicagel using dichloromethane and hexane as eluent to give white colour solid of $[\text{L}(\text{CO})_3\text{Re}(\mu\text{-SR})_2\text{Re}(\text{CO})_3\text{L}]$ metallacycles.

3.3. *cis*–[$\text{L}(\text{CO})_3\text{Re}(\mu\text{-SC}_6\text{H}_5)_2\text{Re}(\text{CO})_3\text{L}$] [$\text{L} = \text{py}$] (**1**)

A mixture of $\text{Re}_2(\text{CO})_{10}$ (196 mg, 0.3 mmol) and diphenyl disulphide (44 mg, 0.2 mmol), were taken in a 50 mL two neck Schlenk flask and fitted with a reflux condenser. The system was evacuated and N_2 was purged. Pyridine (2 ml, 24 mmol) and 30 ml of mesitylene were added under N_2 atmosphere. The reaction mixture was heated to 130 °C under N_2 for 10 h and allowed to cool to room temperature. Some of the settled white solid was separated from the reaction mixture, and the solvent was removed by vacuum distillation. The solid mixture was washed with hexane, chromatographed on silicagel using dichloromethane and hexane as eluent to give white colour solid of *cis*–[$(\text{py})(\text{CO})_3\text{Re}(\mu\text{-SPh})_2\text{Re}(\text{CO})_3(\text{py})$]. Yield: 86 mg, 57% (based on $\text{Re}_2(\text{CO})_{10}$). Anal. Calc. for $\text{C}_{28}\text{H}_{20}\text{N}_2\text{O}_6\text{Re}_2\text{S}_2$: C, 36.67; H, 2.19; N, 3.05. Found: C, 37.33; H, 2.16; N, 3.28%. ^1H NMR (400 MHz, CDCl_3 , ppm): δ 8.96 (d, 4H, H^2 (py), $^3\text{J} = 6.4$ Hz), 7.79 (d, 4H, H^2 (ph), $^3\text{J} = 8.0$ Hz), 7.64 (t, 2H, H^4 (py), $^3\text{J} = 7.6$ Hz), 7.34 (t, 4H, H^3 (py), $^3\text{J} = 7.6$ Hz); 7.17 (t, 4H, H^3 (ph), $^3\text{J} = 6.4$ Hz), 7.12 (t, 2H, H^4 (ph), $^3\text{J} = 6.4$ Hz). ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ 198.8, 195.0 (1:2, CO), 155.3, 138.8, 124.7 (py), 137.5, 131.4, 128.6, 125.9 (ph). UV–Vis. (CH_2Cl_2 , λ nm (ϵ) $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$): 229 (32,100), 268 (35,150). Emission: $\lambda_{\text{max}}^{\text{em}}$ (CH_2Cl_2)/(nm) 373. IR (CH_2Cl_2): $\nu_{(\text{CO})}$ 2027 (m) 1927 (m) 1904 (vs) cm^{-1} .

3.4. *cis*–[$\text{L}(\text{CO})_3\text{Re}(\mu\text{-SC}_6\text{H}_5)_2\text{Re}(\text{CO})_3\text{L}$] [$\text{L} = \text{pic}$] (**2**)

Compound **2** was prepared using $\text{Re}_2(\text{CO})_{10}$ (196 mg, 0.3 mmol), diphenyl disulphide (44 mg, 0.2 mmol) and 4-picoline (2 ml, 20 mmol) in mesitylene (30 ml) following the procedure adopted for **1**. It was isolated as a white solid of *cis*–[$\text{pic}(\text{CO})_3\text{Re}(\mu\text{-SC}_6\text{H}_5)_2\text{Re}(\text{CO})_3\text{pic}$]. Yield: 36 mg, 25% (based on $\text{Re}_2(\text{CO})_{10}$). Anal. Calc. for $\text{C}_{30}\text{H}_{24}\text{N}_2\text{O}_6\text{Re}_2\text{S}_2$: C, 38.13; H, 2.56; N, 2.96. Found: C, 38.08; H, 2.53; N, 2.92%. ^1H NMR (400 MHz, CDCl_3 , ppm): δ 8.85 (d, 4H, H^2 (pic), $^3\text{J} = 6.8$ Hz), 7.36 (t, H^3 4H, (ph), $^3\text{J} = 7.6$ Hz); 7.85 (d, 4H, H^2 (ph), $^3\text{J} = 8.4$ Hz), 7.24 (d, 4H, H^3 (pic), $J = 7.2$ Hz); 7.19 (t, 2H, H^4 (ph), $^3\text{J} = 7.2$ Hz), 2.45 (s, 6H, CH_3 (pic)). ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ 195.2, 182.4 (1:2, CO), 154.8, 149.5, 125.4, 21.1 (pic), 139.0, 131.5, 128.5, 125.8 (ph). UV–Vis. ($\lambda_{\text{max}}^{\text{ab}}$ (CH_2Cl_2)/(nm) (ϵ) $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$): 228 (47,850), 265 (33,800). Emission: $\lambda_{\text{max}}^{\text{em}}$ (CH_2Cl_2)/(nm) 370. IR (CH_2Cl_2): $\nu_{(\text{CO})}$ 2027 (m) 2012 (s) 1924 (m) 1903 (vs) cm^{-1} .

3.5. *cis*-[L (CO)₃Re(μ -SC₆H₅)₂Re(CO)₃ L] [L = Phpy] (3)

Compound **3** was prepared using Re₂(CO)₁₀ (196 mg, 0.3 mmol), diphenyl disulphide (66 mg, 0.3 mmol) and 4-phenylpyridine (47 mg, 0.3 mmol) in mesitylene (30 ml) following the procedure adopted for **1**. It was isolated as a pale yellow solid of *cis*-[Phpy-(CO)₃Re(μ -SC₆H₅)₂Re(CO)₃Phpy]. Yield: 43 mg, 36% (based on Re₂(CO)₁₀). Anal. Calc. for C₄₀H₂₈N₂O₆Re₂S₂: C, 44.93; H, 2.64; N, 2.62. Found: C, 44.68; H, 2.68; N, 2.58%. ¹H NMR (400 MHz, CDCl₃, ppm): δ 9.01 (d, 4H, H² (Phpy), ³J = 6.4 Hz), 7.85 (d, 4H, H² (ph), ³J = 8.4 Hz), 7.38 (t, 4H, H³ (Phpy), ³J = 7.2 Hz), 7.31 (m, 14H, Phpy & ph), 7.20 (t, 2H, H⁴ (Phpy), ³J = 7.6 Hz). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 198.4, 195.0 (1:2, CO), 155.5, 149.8, 138.9, 131.5, 130.2, 126.6, 121.9 (Phpy), 135.4, 129.3, 128.6, 125.9 (ph). UV-Vis. { $\lambda_{\text{max}}^{\text{ab}}$ (CH₂Cl₂)/(nm) (ϵ) dm³ mol⁻¹ cm⁻¹}: 226 (45,250), 264 (49,700), 358 (7,950). Emission: $\lambda_{\text{max}}^{\text{em}}$ (CH₂Cl₂)/(nm) 402. IR (CH₂Cl₂): $\nu_{(\text{CO})}$ 2026 (m) 2011 (vs) 1924 (m) 1902 (vs) cm⁻¹.

3.6. *cis*-[L (CO)₃Re(μ -SC₆H₄CH₃)₂Re(CO)₃ L] [L = py] (4)

Compound **4** was prepared using Re₂(CO)₁₀ (196 mg, 0.3 mmol), *p*-tolyl disulphide (49 mg, 0.2 mmol), and pyridine (2 ml, 24 mmol) in mesitylene (30 ml) following the procedure adopted for **1**. It was isolated as a white solid of *cis*-[py(CO)₃Re(μ -SC₆H₄CH₃)₂Re(CO)₃py]. Yield: 120 mg, 49% (based on Re₂(CO)₁₀). Anal. Calc. for C₃₀H₂₄N₂O₆Re₂S₂: C, 39.49; H, 2.9; N, 2.87. Found: C, 38.67; H, 2.68; N, 2.77%. ¹H NMR (400 MHz, CD₃COCD₃, ppm): δ 9.03 (d, 4H, H² (py), ³J = 6.4 Hz), 7.92 (t, 2H, H⁴ (py), ³J = 7.6 Hz), 7.75 (d, 4H, H² (ph), ³J = 8.4 Hz), 7.41 (dt, 4H, H³ (py), ³J = 5.6 Hz), 7.19 (d, 4H, H³ (ph), ³J = 8.0 Hz), 2.34 (s, 6H, CH₃ (*p*-tolyl)). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 198.8, 194.0 (1:2, CO), 154.3, 136.4, 124.3 (py), 130.7, 134.6, 130.3, 128.2 (ph), 19.8 (CH₃, (*p*-tolyl)). UV-Vis. { $\lambda_{\text{max}}^{\text{ab}}$ (CH₂Cl₂)/(nm) (ϵ) dm³ mol⁻¹ cm⁻¹}: 229 (40,150), 265 (29,950). Emission: $\lambda_{\text{max}}^{\text{em}}$ (CH₂Cl₂)/(nm) 375. IR (CH₂Cl₂): $\nu_{(\text{CO})}$ 2027 (m) 2012 (s) 1923 (m) 1904 (vs) cm⁻¹.

3.7. *cis*-[L (CO)₃Re(μ -SC₆H₄CH₃)₂Re(CO)₃ L] [L = pic] (5)

Compound **5** was prepared using Re₂(CO)₁₀ (196 mg, 0.3 mmol), *p*-tolyl disulphide (49 mg, 0.2 mmol), and 4-picoline (2 ml, 20 mmol) in mesitylene (30 ml) following the procedure adopted for **1**. It was isolated as a white solid of *cis*-[pic(CO)₃Re(μ -SC₆H₄CH₃)₂Re(CO)₃pic]. Yield: 56 mg, 19% (based on Re₂(CO)₁₀). Anal. Calc. for C₃₂H₂₈N₂O₆Re₂S₂: C, 39.49; H, 2.9; N, 2.87. Found: C, 38.67; H, 2.81, N, 2.83%. ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.77 (d, 4H, H² (pic), ³J = 6.4 Hz), 7.66 (d, 4H, H² (ph), ³J = 8.4 Hz), 7.14 (d, 4H, H³ (ph), ³J = 8.0 Hz), 6.90 (d, 4H, H³ (pic), ³J = 6.4 Hz), 2.34 (s, 6H, CH₃ (pic)). 2.33 (s, 6H, CH₃ (*p*-tolyl)). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 198.7, 195.2 (1:2, CO), 154.7, 152.9, 125.3, 21.0 (pic), 149.4, 135.5, 131.3, 129.3, (ph), 20.8 (CH₃, (*p*-tolyl)). UV-Vis. { $\lambda_{\text{max}}^{\text{ab}}$ (CH₂Cl₂)/(nm) (ϵ) dm³ mol⁻¹ cm⁻¹}: 233 (11,850), 266 (20,500). Emission: $\lambda_{\text{max}}^{\text{em}}$ (CH₂Cl₂)/(nm) 280, 304. IR (CH₂Cl₂): $\nu_{(\text{CO})}$ 2025 (s) 2009 (vs) 1921 (w) 1902 (s) cm⁻¹.

3.8. *cis*-[L (CO)₃Re(μ -SC₆H₄CH₃)₂Re(CO)₃ L] [L = Phpy] (6)

Compound **6** was prepared using Re₂(CO)₁₀ (130 mg, 0.2 mmol), *p*-tolyl disulphide (49 mg, 0.2 mmol), and 4-phenylpyridine (31 mg, 0.2 mmol) in mesitylene (30 ml) following the procedure adopted for **1**. It was isolated as a white solid *cis*-[Phpy(CO)₃-Re(μ -SC₆H₄CH₃)₂Re(CO)₃Phpy]. Yield: 22 mg, 17% (based on Re₂(CO)₁₀). Anal. Calc. for C₄₂H₃₂N₂O₆Re₂S₂: C, 45.97; H, 2.94; N, 2.55. Found: C, 45.87; H, 2.85, N, 2.63%. ¹H NMR (400 MHz, CDCl₃, ppm): δ 9.0 (d, 4H, H² (phpy), ³J = 6.8 Hz), 7.73 (d, 4H, H² (Phpy), ³J = 8.0 Hz), 7.38 (t, 4H, H³ (Phpy), ³J = 7.2 Hz), 7.32 (d, 4H, H² (ph), ³J = 8.4 Hz), 7.19 (d, 4H, H³ (ph), ³J = 8.0 Hz), 7.29 (m, 6H, H³

& H⁴ (Phpy)), 2.37 (s, 6H, CH₃ (*p*-tolyl)). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 198.9, 195.3 (1:2, CO), 155.6, 149.9, 135.7, 130.3, 129.5, 126.7, 122.0 (Phpy), 135.7, 135.5, 131.4, 129.5 (ph), 21.1 (CH₃, (*p*-tolyl)). UV-Vis. { $\lambda_{\text{max}}^{\text{ab}}$ (CH₂Cl₂)/(nm) (ϵ) dm³ mol⁻¹ cm⁻¹}: 226 (45,250), 264 (49,700), 358 (7,950). Emission: $\lambda_{\text{max}}^{\text{em}}$ (CH₂Cl₂)/(nm) 402. IR (CH₂Cl₂): $\nu_{(\text{CO})}$ 2026 (m) 2011 (vs) 1924 (m) 1902 (vs) cm⁻¹.

3.9. *cis*-[L (CO)₃Re(μ -SCH₂C₆H₅)₂Re(CO)₃ L] [L = py] (7)

Compound **7** was prepared using Re₂(CO)₁₀ (196 mg, 0.3 mmol), dibenzyl disulphide (49 mg, 0.2 mmol), and pyridine (2 ml, 24 mmol) in mesitylene (30 ml) following the procedure adopted for **1**. It was isolated as a white solid of *cis*-[py(CO)₃Re(μ -SCH₂C₆H₅)₂Re(CO)₃py]. Yield: 108 mg, 62% (based on Re₂(CO)₁₀). Anal. Calc. for C₃₀H₂₄N₂O₆Re₂S₂: C, 38.13; H, 2.55; N, 2.96. Found: C, 37.98; H, 2.60; N, 2.91%. ¹H NMR (400 MHz, CD₃COCD₃, ppm): δ 8.75 (d, 4H, H² (py), ³J = 6.8 Hz), 7.76 (tt, 2H, H⁴ (py), ³J = 7.6 Hz), 7.54 (d, 4H, H² (ph), ³J = 7.8 Hz), 7.34 (t, 4H, H³ (py), ³J = 7.6 Hz), 7.26 (m, H³ & H⁴ (ph), 6H), 4.43 (s, 4H, CH₂ (benz)). ¹³C NMR (100 MHz, CD₃COCD₃, ppm): δ 201.5, 195.2 (1:2, CO), 155.7, 142.6, 126.2 (py), 139.3 129.6, 129.4, 127.9 (ph), 43.6 (CH₂, (benz)). UV-Vis. { $\lambda_{\text{max}}^{\text{ab}}$ (CH₂Cl₂)/(nm) (ϵ) dm³ mol⁻¹ cm⁻¹}: 228 (34,350), 267 (12,700). Emission: $\lambda_{\text{max}}^{\text{em}}$ (CH₂Cl₂)/(nm) 369. IR (CH₂Cl₂): $\nu_{(\text{CO})}$ 2021 (m) 2006 (s) 1913 (m) 1900 (vs) cm⁻¹.

3.10. *cis*-[L (CO)₃Re(μ -SCH₂C₆H₅)₂Re(CO)₃ L] [L = pic] (8)

Compound **8** was prepared using Re₂(CO)₁₀ (196 mg, 0.3 mmol), dibenzyl disulphide (49 mg, 0.2 mmol), and 4-picoline (2 ml, 20 mmol) in mesitylene (50 ml) following the procedure adopted for **1**. It was isolated as a white solid of *cis*-[pic(CO)₃Re(μ -SCH₂C₆H₅)₂Re(CO)₃pic]. Yield: 34 mg, 25% (based on Re₂(CO)₁₀). Anal. Calc. for C₃₂H₂₈N₂O₆Re₂S₂: C, 39.49; H, 2.90; N, 2.87. Found: C, 39.61; H, 2.85; N, 2.89%. ¹H NMR (400 MHz, CD₃COCD₃, ppm): δ 8.57 (d, 4H, H² (pic), ³J = 6.4 Hz), 7.52 (d, 4H, H² (ph), ³J = 7.2 Hz), 7.33 (t, 4H, H³ (ph), ³J = 7.2 Hz), 7.26 (tt, 2H, H⁴ (ph), ³J = 7.2 Hz), 7.09 (d, 4H, H³ (pic), ³J = 6.6 Hz), 4.42 (s, 4H, CH₂ (benz)), 2.37 (s, 6H, CH₃ (pic)). ¹³C NMR (100 MHz, CD₃COCD₃, ppm): δ 201.7, 195.3 (1:2, CO), 155.1, 151.3, 126.8 (pic), 142.7, 129.6, 129.4, 127.8 (ph), 43.5 (CH₂, (benz)), 21.1 (CH₃, (pic)). UV-Vis. { $\lambda_{\text{max}}^{\text{ab}}$ (CH₂Cl₂)/(nm) (ϵ) dm³ mol⁻¹ cm⁻¹}: 228 (31,400), 269 (11,150). Emission: $\lambda_{\text{max}}^{\text{em}}$ (CH₂Cl₂)/(nm) 366. IR (CH₂Cl₂): $\nu_{(\text{CO})}$ 2019 (m) 2004 (s) 1913 (m) 1898 (vs) cm⁻¹.

3.11. *cis*-[L (CO)₃Re(μ -SCH₂C₆H₅)₂Re(CO)₃ L] [L = Phpy] (9)

Compound **9** was prepared using Re₂(CO)₁₀ (196 mg, 0.3 mmol), dibenzyl disulphide (74 mg, 0.3 mmol), and 4-phenylpyridine (47 mg, 0.3 mmol) in mesitylene (30 ml) following the procedure adopted for **1**. It was isolated as a pale yellow solid of *cis*-[Phpy-(CO)₃Re(μ -SCH₂C₆H₅)₂Re(CO)₃Phpy]. Yield: 16 mg, 10% (based on Re₂(CO)₁₀). Anal. Calc. for C₄₂H₃₂N₂O₆Re₂S₂: C, 45.97; H, 2.94; N, 2.55. Found: C, 45.08; H, 2.73; N, 2.43%. ¹H NMR (400 MHz, CD₃COCD₃, ppm): δ 8.76 (d, 4H, H² (Phpy), ³J = 6.4 Hz), 7.60 (d, 4H, H² (Phpy), ³J = 8.4 Hz), 7.42 (t, 4H, H³ (Phpy), ³J = 6.8 Hz), 7.36 (d, 4H, H² (benzyl), ³J = 6.0 Hz), 7.26 (m, H³ (Phpy & benzyl), 10H), 4.51 (s, 4H, CH₂ (benz)). ¹³C NMR (100 MHz, CD₃COCD₃, ppm): δ 200.4, 194.4 (1:2, CO), 155.2, 149.3, 135.4, 130.0, 129.2, 126.4, 121.7 (Phpy), 141.9, 129.0, 128.6, 127.0 (ph), 42.9 (CH₂, (benz)). UV-Vis. { $\lambda_{\text{max}}^{\text{ab}}$ (CH₂Cl₂)/(nm) (ϵ) dm³ mol⁻¹ cm⁻¹}: 229 (32,100), 268 (35,150), 348 (960). Emission: $\lambda_{\text{max}}^{\text{em}}$ (CH₂Cl₂)/(nm) 389. IR (CH₂Cl₂): $\nu_{(\text{CO})}$ 2020 (s) 2005 (vs) 1914 (m) 1900 (vs) cm⁻¹.

3.12. Crystal structure determinations

Crystals of **4**, **8** and **9** suitable single crystal for X-ray crystallography were grown by slow diffusion of hexane into CH_2Cl_2 solution. Single crystal X-ray structural studies were performed on Oxford Diffraction XCALIBUR-S CCD equipped diffractometer with an Oxford Instruments low-temperature attachment. Data were collected at 150(2) K using graphite-monochromated Mo $\text{K}\alpha$ radiation ($\lambda_{\alpha} = 0.71073 \text{ \AA}$). The strategy for the Data collection was evaluated by using the CrysAlisPro CCD software. The data were collected by the standard 'phi-omega scan' techniques, and were scaled and reduced using CrysAlisPro RED software. The structures were solved by direct methods using SHELXS-97 and refined by full matrix least squares with SHELXL-97 [62], refining on F^2 . The positions on all the atoms were obtained by direct methods. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in geometrically constrained positions and refined with isotropic temperature factors, generally $1.2 \times U_{\text{eq}}$ of their parent atoms.

4. Conclusion

In this article, we have described a simple and efficient method to synthesize sulphur bridged dinuclear Re(I) metallacycles from $\text{Re}_2(\text{CO})_{10}$, diaryl disulphides and with few monodentate pyridine ligands in mesitylene medium. The molecular structure of compounds **4**, **8** and **9** have been elucidated by single crystal X-ray diffraction analysis. The pyridyl groups attached to rhenium centers are oriented in a *cis* conformation and stabilized by π – π stacking interaction. The novel metallacycles having a shape of a molecular tweezers would be useful for molecular recognition studies.

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Appendix A. Supplementary material

CCDC 756132, 756131, and 756133 contain the supplementary crystallographic data for **4**, **8** and **9**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorgchem.2010.02.027.

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