SUPPORTING INFORMATION

Re(I)-nitroxide complexes

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1ESI. General Procedures

The (η^5-cyclopentadienyl)tricarbonylrhenium(I) **[(Cp)Re(CO)$_3$]**[1], (η^5-formylcyclopentadienyl)tricarbonylrhenium(I) **[(CHOCp)Re(CO)$_3$]**[2] and 2,3-bis(hydroxyamino)-2,3-dimethylbutane (**BHA**)[3] were synthesized by the known procedures. The commercially available reagents and solvents for synthesis under Ar, electrochemical measurements and EPR study were purified, dried and degassed following standard literature methods[4] and/or using a MBRAUN MB SPS-800 system. The reactions were monitored by TLC using «Alugram SIL G/UV254» and «POLYGRAM ALOX N/UV254» ("Macherey-Nagel") sheets. Column chromatography was carried out with the use of SiO$_2$ «0.04-0.0063 mm / 230-400 mersh ASTM for column chromatography ("Macherey-Nagel") and Al$_2$O$_3$ of chromatographic grade purchased from the Donetsk Plant of Chemical Reagents. The IR spectra of the samples pelletized with KBr were recorded on a «VECTOR-22» (Bruker, Karlsruhe, Germany). The melting points were determined on a melting point apparatus "Stuart" (SMP3). The microanalyses were performed on a «EURO EA3000» CHNS analyser (HEKAtech, Webberg, Germany) at the Chemical Analytical Center of the Novosibirsk Institute of Organic Chemistry SB RAS.

2ESI. Synthesis of spin-labeled cyrhetrenes and their diamagnetic precursor

[(CHOCp)Re(CO)$_3$]   [(BHACp)Re(CO)$_3$]   [(NNCp)Re(CO)$_3$]   [(INCp)Re(CO)$_3$]
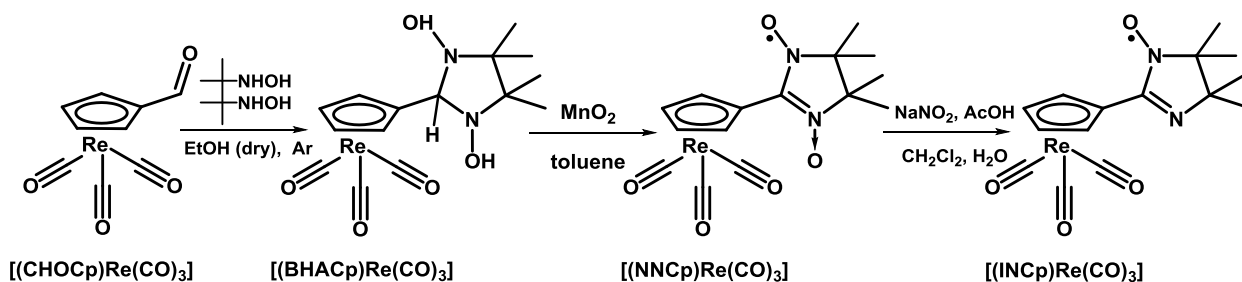
[(BHACp)Re(CO)$_3$] 2-(η^5-cyclopentadienyl)tricarbonylrhenium(I)-4,4,5,5-tetramethylimidazolidine-1,3-diole. The mixture of freshly obtained **[(CHOCp)Re(CO)$_3$]** (0.248 g; 0.68 mmol) and **BHA** (0.200 g; 1.35 mmol) in dry EtOH (10 mL) was kept under Ar at room temperature for 72 h. Then EtOH was evaporated, and the colorless residue was purified by column chromatography (Al$_2$O$_3$ 1.5×15 cm, Et$_2$O:n-C$_6$H$_{14}$ = 1:1 mixture as an eluent), followed by recrystallization from a Et$_2$O:n-C$_6$H$_{14}$ mixture. Yield: 0.315 g (93%), colorless agglomerates of elongated prismatic crystals. Mp 171-175 °C (decomp). IR spectrum (KBr) ν: 2983, 2019, 1904, 1634, 1467, 1415, 1366, 1163, 1030, 995, 827, 599, 509 cm^{-1}. Found (%): C, 36.6; H, 4.2; N, 5.6. Calculated for C$_{15}$H$_{19}$N$_2$O$_5$Re (%): C, 36.5; H, 3.9; N, 5.7.

[(NNCp)Re(CO)$_3$]-**III** 2-(η^5-cyclopentadienyl)tricarbonylrhenium(I)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazole-3-oxide-1-oxyl. MnO$_2$ (1.00 g) was added to a solution of

[(BHACp)Re(CO)$_3$] (0.203 g; 0.41 mmol) in toluene (~20 mL) and the mixture was stirred for ~1 h at the water bath. Then resulted dark-blue solution was filtered, the filtrate was evaporated, and the residue was purified by column chromatography (Al$_2$O$_3$ 1.5×15 cm, Et$_2$O as an eluent). Gradual concentration of a CH$_2$Cl$_2$:n-C$_6$H$_{14}$ = 1:5 solution by solvents evaporation from open flask at 15 °C gave aggregates of dark blue elongated prismatic crystals. Yield: 0.090 g (45%), dark-blue. Mp 141-143 °C (decomp). Found (%): C, 37.1; H, 3.2; N, 5.7. Calculated for C$_{15}$H$_{16}$N$_2$O$_5$Re (%): C, 36.7; H, 3.3; N, 5.7.

Dark-blue prismatic crystals of **[(NNCp)Re(CO)$_3$]-II** polymorphic modification were obtained by slow recrystallization of **[(NNCp)Re(CO)$_3$]** from dry EtOH at 4 °C. Mp 141-143 °C (decomp). Found (%): C, 37.0; H, 3.2; N, 5.8. Calculated for C$_{15}$H$_{16}$N$_2$O$_5$Re (%): C, 36.7; H, 3.3; N, 5.7.

[(NNCp)Re(CO)$_3$]-I polymorphic modification was obtained by fast concentration of an CH$_2$Cl$_2$:n-C$_6$H$_{14}$= 1:5 solution by solvents removal with a flow of Ar passed over the surface of the solution. The resulted dark-blue needle crystals were quickly filtered a few minutes later after their precipitation. Note that if the crystals of **[(NNCp)Re(CO)$_3$]-I** are stored under solution for prolonged time, they completely recrystallize to crystals of **[(NNCp)Re(CO)$_3$]-III**. Mp 145-146 °C (decomp). Found (%): C, 37.4; H, 3.2; N, 5.6. Calculated for C$_{15}$H$_{16}$N$_2$O$_5$Re (%): C, 36.7; H, 3.3; N, 5.7.

All polymorphic modifications of **[(NNCp)Re(CO)$_3$]** soluble in aromatic hydrocarbons, halogen-substituted hydrocarbons, acetone, Et$_2$O, alcohols, moderately soluble in saturated hydrocarbons, insoluble in water. IR spectrum (KBr) ν: 2997, 2024, 1923, 1562, 1454, 1426, 1395, 1370, 1140, 1033, 868, 596, 511 cm^{-1}.

[(INCp)Re(CO)$_3$] 2-(η^5-cyclopentadienyl)tricarbonylrhenium(I)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazole-1-oxyl. A mixture of **[(NNCp)Re(CO)$_3$]** (0.120 g, 0.25 mmol), NaNO$_2$ (0.034 g; 0.49 mmol), AcOH (0.600 mL) in CH$_2$Cl$_2$ (10 mL) and H$_2$O (0.400 mL) was stirred until the starting **[(NNCp)Re(CO)$_3$]** was completely consumed (after ~10 min according to TLC). Then, the mixture was quenched by adding NaHCO$_3$ and dried with anhydrous Na$_2$SO$_4$. After filtration the resulted orange solution was evaporated, and the residue was purified by column chromatography (Al$_2$O$_3$ 1.5×15 cm, Et$_2$O as an eluent). The product was recrystallized from a Et$_2$O:n-C$_6$H$_{14}$ mixture. Yield: 58 mg (69%), orange elongated plates. **[(INCp)Re(CO)$_3$]** soluble in aromatic hydrocarbons, halogen-substituted hydrocarbons, saturated hydrocarbons, acetone, Et$_2$O, alcohols, insoluble in water. Mp 115-117 °C (decomp). IR spectrum (KBr) ν: 2984, 2024, 1928, 1584, 1460, 1409, 1368, 1161, 1040, 830, 594, 512 cm^{-1}. Found (%): C, 38.1; H, 3.7; N, 5.9. Calculated for C$_{15}$H$_{16}$N$_2$O$_4$Re (%): C, 38.0; H, 3.4; N, 5.9.

3ESI. EPR Spectroscopy

Continuous wave (CW) X-band (9.88 GHz) EPR measurements were carried out on a Bruker EMX spectrometer at room temperature. Spectra were recorded at a microwave power of ~2 mW and a modulation amplitude of 0.01 mT at 100 kHz. Diluted toluene solutions of [(NNCp)Re(CO)$_3$] and [(INCp)Re(CO)$_3$] (~10^{-3} mM) were studied; samples were preliminarily degassed by freeze–pump–thaw cycles. EPR data were simulated with the *EasySpin* toolbox.[5]

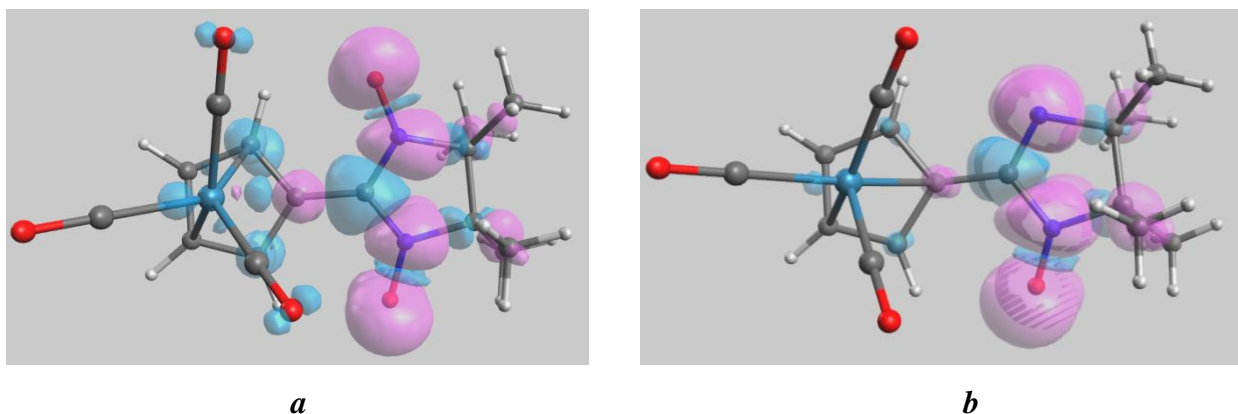*a*   *b*

Figure S1. DFT (ORCA 4.2[6] LC-BLYP/def2-TZVPP) calculated spin density surfaces (ρ_s=0.001, pink - positive, blue - negative) for [(NNCp)Re(CO)$_3$] (*a*) and [(INCp)Re(CO)$_3$] (*b*). The total Mulliken spin density values localized on {O←N=C–N–•O}/{N=C–N–•O} fragments are 1.04 for [(NNCp)Re(CO)$_3$] and 1.00 for [(INCp)Re(CO)$_3$] and at rhenium(I) center are -0.017 for [(NNCp)Re(CO)$_3$] and -0.006 for [(INCp)Re(CO)$_3$].

4ESI. Cyclic Voltammetry

Cyclic voltammetry (CV) measurements were performed with a PC-piloted digital potentiostat IPC-Pro-MF (Econix). The experiments were carried out in a 10-mL five-neck glass conic electrochemical cell equipped with a water jacket for thermostating. As a working electrode, glass carbon (GC) disk (d = 1.7 mm) was used, polished before each run; a platinum wire was used as an auxiliary electrode. The potentials are referred to the AgCl/KCl$_{sat}$ electrode separated from the analyte by an electrolytic bridge filled with supporting electrolyte (0.1 M Bu$_4$NBF$_4$/MeCN). Solution deaeration was carried out by purging them with highly pure argon before recording every CV curve and argon passing over it for the duration of the experiments. The approximation to zero current of the potentials of cathodic and anodic peaks to the determination of half-wave potentials $E^{0'}$ was carried out as described elsewhere.[7]
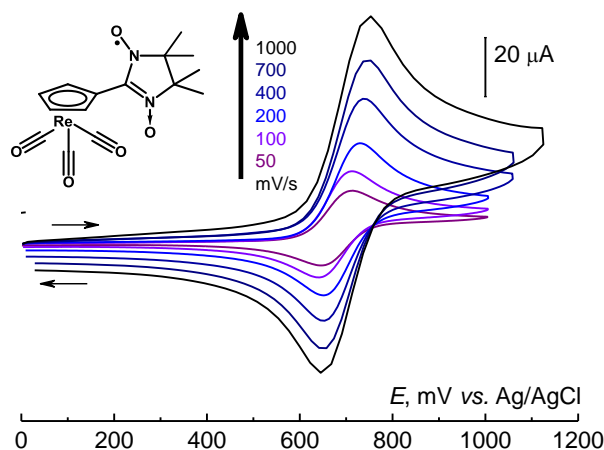
Figure S2. CV curves of [(NNCp)Re(CO)$_3$] solution in MeCN (2.5·10^{-3} M) at different scan rates of potential application (a GC disk electrode d = 1.7 mm, supporting electrolyte 0.1 M Bu$_4$NBF$_4$/MeCN, T = 298 K). The shape of the CV curves, the ratio of the currents of the anode and the cathode peaks and the apparent number of electrons (n$_{app}$ ~ 1) are independent on the 50-1000 mV·s^{-1} scan rate of application of potentials.

a

b

c
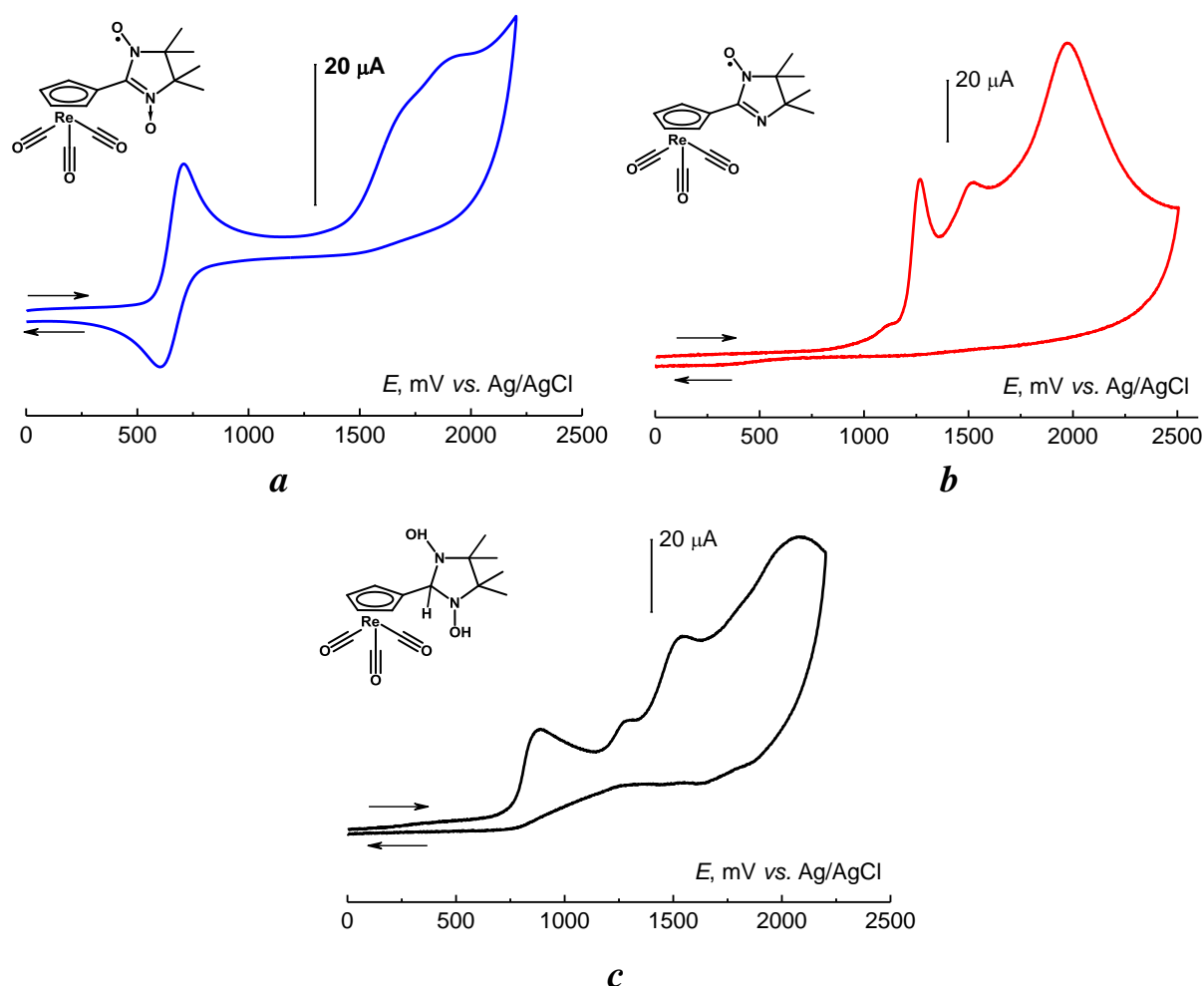
Figure S3. CV curves of [(NNCp)Re(CO)$_3$] (a; 2.5·10^{-3} M), [(INCp)Re(CO)$_3$] (b; 5.0·10^{-3} M) [(BHACp)Re(CO)$_3$] (c; 5.0·10^{-3} M) solutions in MeCN (a GC disk electrode d = 1.7 mm, supporting electrolyte 0.1 M Bu$_4$NBF$_4$/MeCN, the scan rate of application of potentials 100 mV·s^{-1}, T = 298 K).

5ESI. Single crystals X-ray Crystallography

The intensity data for single crystals were collected on Bruker AXS diffractometers – a SMART APEX II (Mo Kα radiation) and an APEX DUO (Cu Kα radiation) with a Cobra low-temperature accessory (Oxford Cryosystem). The structures were solved by direct methods and refined by full-matrix least-squares in an anisotropic approximation for all non-hydrogen atoms. The H atoms were calculated geometrically and refined in a riding model. All calculations on structure solution and refinement were performed with SHELXL (2016/4 and 2018/3) software. Crystallographic data, selected bond lengths, angles and intermolecular distances can be found in Tables S1, S2 of ESI and Table 1 of main text.
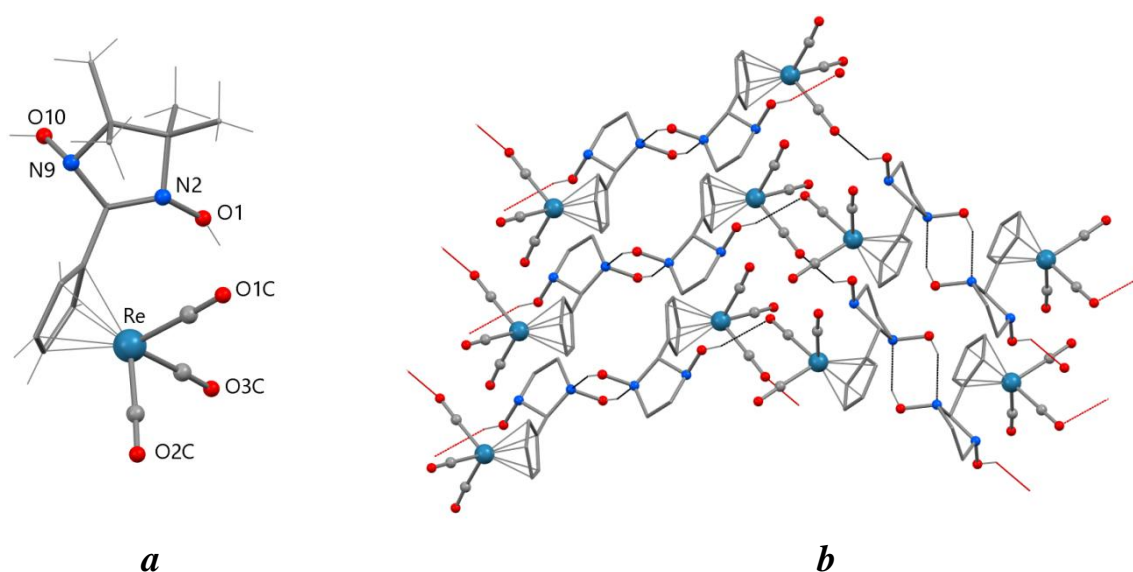

a *b*

Figure S4. [(BHACp)Re(CO)$_3$]: (*a*) molecular structures; (*b*) a fragment of *H*-bonded layer - the H atoms, the geminal CH$_3$ groups are omitted for clarity, *H*-bonds shown as thin dark gray lines.

The imidazolidine ring of [(BHACp)Re(CO)$_3$] adopts an envelope conformation. The angle between the planes of the Cp ring and {CN$_2$} fragment of the imidazolidine cycle is 77.8° (Table S2), both OH groups are located on the one side of the imidazolidine cycle. The N–O distances (1.439(5) and 1.451(4) Å) are slightly longer than those typical of sterically hindered hydroxylamines (~1.39-1.41 Å)[8] due to the formation of hydrogen bonds. Hydroxyl groups are linked to different neighboring [(BHACp)Re(CO)$_3$] molecules by H-bonds between NOH-fragments (O10…N9 = 2.891(5) Å) and with CO ligand (O1…O1C = 3.031(6) Å), connecting the molecules into a layer.

Table S1. Crystal data and experimental details

| Compound | [(BHACp)Re(CO)$_3$] | [(NNCp)Re(CO)$_3$] | | | [(INCp)Re(CO)$_3$] |
		I	II	III	
FW	493.52		490.50		474.50
T, K	240	296	296	296	240
Space group, Z	$P2_1/n$, 4	$P2_1/c$, 4	$P\bar{1}$, 4	$P2_1/n$, 8	$P2_1/c$, 4
a, b, c, Å	10.3946(4) 7.1672(3) 22.2958(8)	11.8875(4) 10.0482(3) 14.1283(4)	10.382(4) 10.503(4) 16.360(6)	17.0007(3) 10.2467(2) 20.5719(4)	6.8520(3) 24.5256(9) 10.3668(4)
α, β, γ, °	94.282(1)	92.488(2)	80.32(3) 80.44(3) 74.62(2)	110.439(1)	108.523(2)
V, Å^3	1656.40(11)	1686.01(9)	1681.5(11)	3358.04(11)	1651.89(11)
D_c, g cm^{-3}	1.979	1.932	1.938	1.940	1.908
θ_{max}, deg.	67.560	28.375	28.471	28.327	67.915
I_{hkl} (meas/uniq) R_{int}	12840 / 2966 0.0348	15336 / 4179 0.0882	11478 / 8295 0.4019	31900 / 8308 0.1263	13367 / 2978 / 0.0546
I_{hkl} ($I>2\sigma_I$) / Ns	2918 / 219	1825 / 225	3512 / 415	4704 / 415	2749 / 208
$GooF$	1.249	0.8351	0.839	0.915	1.041
R_1 / wR_2 ($I>2\sigma_I$)	0.0274 / 0.0672	0.0419 / 0.0762	0.0838 / 0.1849	0.0492 / 0.1110	0.0343 / 0.0969
$CCDC$	2064834	2064832	2064833	2064835	2064831

Table S2. Selected bond lengths (Å) and angles (°)

Compound		Re–C_CO	Re–C_Cp (Re–centroid)	N–O	∠Cp–{CN_2(O_2)}	C_Cp–C_NN
$[(BHACp)Re(CO)_3]$		1.907(5), 1.912(5), 1.923(5)	2.296(4)–2.315(4) (1.949)	1.439(5), 1.451(4)	77.8	1.515(6)
$[(NNCp)Re(CO)_3]$	I	1.885(9), 1.889(9), 1.910(8)	2.281(8)–2.322(8) (1.954)	1.257(6), 1.271(6)	3.0	1.436(8)
	IIa	1.870(17), 1.930(21), 1.948(18)	2.285(10)–2.345(12) (1.972)	1.291(16), 1.297(15)	4.5	1.46(2)
	IIb	1.860(17), 1.908(15), 1.92(2)	2.289(10)–2.327(11) (1.964)	1.293(14), 1.289(15)	6.7	1.39(2)
	IIIa	1.869(11), 1.921(12), 1.911(11)	2.290(8)–2.311(8) (1.958)	1.282(9), 1.281(8)	4.6	1.483(11)
	IIIb	1.870(12), 1.923(11), 1.920(10)	2.289(8)–2.303(8) (1.953)	1.277(8), 1.285(8)	30.3	1.450(11)
$[(INCp)Re(CO)_3]$		1.893(8), 1.903(6), 1.912(7)	2.294(5)–2.315(6) (1.958)	1.205(6)	7.4	1.452(7)

7ESI. Quantum-Chemical Calculations

Molecular DFT calculations with optimized geometries of the complexes were carried out with ORCA 4.2 quantum chemistry package[6] using range-separated LC-BLYP functional and def2-TZVPP basis set. The spin density is found to be mainly localized on {O←N=C-N-•O}/{N=C-N-•O} fragments of nitroxide-substituted cyrhetrens and has a very small value at rhenium(I) center (Fig. S1). The investigation of a possibility of intramolecular electron transfer for [(NNCp)Re(CO)$_3$] and [(INCp)Re(CO)$_3$] nitroxides have revealed that quintet states (S = 3/2) are the species, that are the closest to ground state of studied complexes. The calculated energy of the resulted spin state isomers is 70 kcal/M and 90 kcal/M higher the ground states of [(NNCp)Re(CO)$_3$] and [(INCp)Re(CO)$_3$], respectively. It makes the thermally induced valence tautomerism or spin transitions unlikely to occur for this type of rhenium(I) complexes with 2-imidazoline nitroxides.

The isotropic exchange parameters (Table 2) were estimated within the broken-symmetry approach of Yamaguchi and co-workers.[9] All periodic DFT+U calculations were performed using the crystallographically determined geometries and an approach based on calculations of similar systems[10] utilizing pseudo-potential PW-SCF code of Quantum Espresso 6.2 package.[11] We used the nonlinear core corrected ultrasoft pseudo-potentials with the PBE exchange-correlation functional. The kinetic energy cutoffs for wave functions and charge density are 50 and 400 Ry, respectively. The integration in the k space was performed over the mesh $2 \times 2 \times 2$ in the first Brillouin zone as in Monkhorst−Pack scheme[12] with a displacement of k-grid at the center of the Brillouin zone and the Gaussian smoothing of 0.136 eV. The Hubbard correlations on Re and O sites were taken into account within the framework of the Dudarev version of GGA+U approach[13] with the values $U_d(Re) = 4.0$ eV,[14] $U_p(O) = 5.0$ eV.[15]

7ESI. Variable-temperature Magnetic Measurements

Magnetic measurements were carried out on an MPMSXL SQUID magnetometer (Quantum Design) in the temperature range 2−300 K in a magnetic field of up to 5 kOe. The paramagnetic components of the magnetic susceptibility χ were determined with allowance for the diamagnetic contribution evaluated from the Pascal constants.[16] The effective magnetic moment was calculated as $\mu_{eff} = [(3k/N_A\mu_B^2)\chi T]^{1/2} \approx (8\chi T)^{1/2}$.

8ESI. REFERENCES

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