Norharmane rhenium(i) polypyridyl complexes: synthesis, structural and spectroscopic characterization†

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Two novel Re(I) complexes with the general formula fac-[Re(CO)₃(L)(nHo)]CF₃SO₃, where L = 2,2'-bipyridine (bpy) or 1,10 phenanthroline (phen) and nHo (9H-pyrido[3,4-b]indole; norharmane) have been synthesized. The Re(I)–nHo complexes were characterized by structural X-ray diffraction, ¹H and ¹³C NMR, UV-vis absorption and FT-IR spectroscopy, and by a combination of two mass spectrometry techniques, namely ESI-MS and UV–MALDI-MS. All characterizations showed that nHo is coordinated to the metal atom by the pyridine nitrogen of the molecule. X-ray structural analysis revealed that the crystal lattices for both complexes are further stabilized by a strong >N–H...O bond between the pyrrole NH group of the pyridoindole ligand and one oxygen atom of the trifluoromethanesulfonate counter-ion. Ground state geometry optimization by DFT calculations showed that in fluid solution the nHo ligand may rotate freely. The nature of the electronic transitions of Re(CO)₃(bpy)(nHo)⁺ were established by TD-DFT calculations. The set of the most important electronic transitions present in this complex are comprised of π → π* electronic transitions centered on bpy and nHo moieties, LLCTnHo → COs, MLLCTRe(CO)₃ → bpy and LLCTnHo → bpy transitions. Additionally, TD-DFT calculations predict the existence of another two intense MLLCTRe(CO)₃ → nHo electronic transitions. Calculated UV-vis absorption spectra are in good agreement with the corresponding experimental data for the bpy-containing complex.

Introduction

β-Carbolines (βCs) are a group of naturally occurring alkaloids structurally derived from 9H-pyrido[3,4-b]indole or norharmane (Scheme 1). In nature, βCs are usually found in plants, algae, animals, and are also endogenously synthesized in mammals.1,2 It has been suggested that these alkaloids would be involved in many biological processes. A large spectrum of psychopharmacological, biological and toxicological activities has been reported for some βCs derivatives, acting as antioxidants, antitumor and antimicrobial agents.3–9 In some neurodegenerative diseases, such as Alzheimer, quaternary βC derivatives (i.e., those methylated in the pyridinic nitrogen) would play a key role.6,7

It is worth mentioning that norharmane, the un-substituted fully aromatic βC, crosses the blood–brain barrier and penetrates into the brain. Inside, norharmane is converted (by certain methyl-transferases) to methyl derivatives exerting significant cytotoxic and neurotoxic effects.8,9

The latter fact seriously reduces the potential medical application of these alkaloids as systemic drugs. Therefore the

Scheme 1  Schematic chemical structure of 9H-pyrido[3,4-b]indole.
search of novel βC derivatives with non-neurotoxic effects is of keen importance. In this regards, the coordination of these alkaloids to transition metal ions through the pyridinic nitrogen of the βC moiety may represent an excellent option deserving further consideration in future studies. The development of transition metal complexes with coordinated bioactive molecules open up new possibilities in drug discovery. In 1998, Al-Allaf et al. synthesized a Pd(n) complex with the natural βC harmine showing great cytotoxic activity against cancer cell lines.10 Recently, Tan et al. synthesized ruthenium(II) transition complexes with norharmane.11 In these complexes, the βC ligand binds to the metal center through the pyridine nitrogen atom. It has been demonstrated that these βC–Ru(n) complexes have nuclear permeability and can induce autophagy and apoptosis in tumor cells lines. These complexes present great anti-proliferative potential and can associate in vitro with DNA. An interesting feature is the enhancement of the βC–Re(I) complexes fluorescence after the intercalation with DNA.12 This “light switch” effect can be used to monitor the intracellular location of the complex inside a cell. However, as far as we know, there are no examples in the literature of βC–Re(I) complexes. This is surprising since Re(i) tricarbonyl complexes, XRe(CO)3L, continue to attract the attention of researchers due to their applicability in broad research areas such as electron transfer studies,13 solar energy conversion,14 catalysis,15 applications as luminescent molecular probes,16 etc. As these complexes show exceptionally rich excited-state behavior and redox chemistry as well as thermal and photochemical stability,17,18 they have also been used as biological labeling reagents and non-covalent probes for bio-molecules and ions.19–21 Furthermore, there are potential biochemical and technical applications based on the formation of adducts between complexes of Re(i) and biological macromolecules such as DNA, proteins or tumor cells.22–26

In order to find novel compounds with potential biomedical applications, we undertake the search of new complexes through the combination of –Re(CO)3 moieties with norharmane. We report here the synthesis of two novel Re(I)–nHo complexes, namely [Re(CO)3(L)(nHo)]+, where L = 2,2’-bipyridine, (1) or 1,10 phenanthroline, (2) along with their structural and spectroscopic characterization.

**Experimental section**

**General**

HPLC grade methanol and acetonitrile (J. T. Baker, USA), were used without further purification. Re(CO)5Cl, 1,10 phenanthroline (phen), norharmane (nHo) and β-cyclo-dextrin (cyclomaltoheptaose) were purchased from Sigma-Aldrich Chemical Co., USA. 2,2’-Bipyridine (bpy) and 2-[(2E)-3-(4-tert-buthylphenyl)-2-methylprop-2-enylidene] malononitrile (DCTB) were purchased from Fluka, Switzerland, toluene from Mallinckrodt Chemicals, tetrahydrofuran (THF) and HClO4 from Merck. Water of very low conductivity (Milli Q grade) was used.

**Instrumentation**

UV-vis absorption spectra were recorded with a Cary 60 UV-vis spectrophotometer (Agilent Technologies) using methanol as solvent. FTIR spectra were recorded with a Nicolet 8700 Thermo Scientific instrument using KBr pellets. 1H NMR and 13C-NMR spectra were recorded at 300 K with a Bruker AM-500 spectrometer operating at 500 MHz. [D6]DMSO was used as solvent and the chemical shift were internally referenced to TMS via (CH3)2SO in (δ = 2.50 ppm). J values are given in Hz.

**Synthesis**

1 and 2 were synthesized in a three-step synthesis (see summary in Fig. 1). First, 180.8 mg of Re(CO)5Cl (0.5 mmol) and 78.1 mg (0.5 mmol) of bpy (for 1), or 90.1 mg (0.5 mmol) of phen (for 2) were suspended in 25 mL of toluene and refluxed for 3 h under N2 atmosphere. After cooling to room temperature, the yellow solid was filtered out and dried under vacuum at 60 °C for 24 h. Later, the solid was dissolved in THF and an equimolar quantity of AgCF3SO3 was added to the solution and the mixture was refluxed for 4 h under N2 atmosphere. Then, it was filtered to remove the AgCl formed during the reaction and the solution was rotaevaporated until dryness.

![Fig. 1: Synthetic path scheme for fac-[Re(CO)3(bpy)(nHo)]+ and fac-[Re(CO)3(phen)(nHo)]+. The fac-[Re(CO)3(bpy)(nHo)]+ protons have been numbered for the NMR analysis.](image-url)
The UV-vis absorption spectra of the pure Re(CO)$_3$(L)-CF$_3$SO$_3$ obtained herein agreed well with the literature spectra. Finally, these compounds were used as precursors to prepare the desired complexes 1 and 2. To this purpose, Re(CO)$_3$(L)CF$_3$SO$_3$ was suspended in 30 ml of methanol with an equimolar quantity of norharnane and refluxed for 8 h under N$_2$ atmosphere. After cooling, the solvent was evaporated until dryness and the resulting solid was dried under vacuum at 60 °C for 48 h. The Re(i)-nHo complexes were dissolved in a minimum volume of dichloromethane and then precipitated by slow addition of cold iso-octane. The re-crystallization procedure was repeated until a constant value for the molar absorption coefficient ($\varepsilon$) was obtained. Chemical yields of 75% (1, 278.8 mg) and 70% (2, 268.7 mg) were obtained in this final step for both complexes. Some Ru(n)-nHo complexes have shown to co-crystallize with solvent molecules. In our case, a co-crystallization of solvent molecules was evident from the elemental analysis results.

fac-[Re(CO)$_3$(bpy)(nHo)]CF$_3$SO$_3$ (1). Found: H, 2.65; C, 43.54; N, 7.05%. C$_{50}$H$_{46}$O$_{6}$N$_{4}$SRe·0.45C$_{8}$H$_{18}$ requires H, 1.71; C, 40.50; N, 5.82%. C 27H16O6F3N4SRe·0.9 CH$_2$Cl$_2$ requires H, 3.06; C, 43.21; N, 7.05%. FT-IR (KBr) ν$_{max}$/cm$^{-1}$ 1915 and 1307 (C4″), 1307 (C4”), 125.3 (C4b), 123.3 (C4a), 121.0(C6), 123.1 (C5), 112.4 (C8) and 762 cm$^{-1}$.

δ$_{C}$(500 MHz, d$_6$-DMSO; TMS) 196.5 (CO), 155.6 (C2′), 154.4 (C2″), 142.3 (C6′), 141.9 (C6″), 141.6 (C5′), 140.4 (C5″), 140.6 (C3′), 136.4 (C9a), 140.6 (C8a), 136.6 (C1), 129.6 (C3′), 129.8 (C3″), 129.6 (C4″), 130.7 (C4”), 130.7 (C7), 125.3 (C4b), 123.3 (C4a), 112.0(C6), 123.1 (C5), 112.4 (C8) and 113.2 ppm (C4).

The Re(i)-nHo complexes were dissolved in methanol/hexane solutions. The measurements of fac-[Re(CO)$_3$(bpy)(nHo)]CF$_3$SO$_3$ crystal were performed on an Oxford Xcalibur, Eos, Gemini CCD diffractometer with graphite-monochromated MoKα ($\lambda = 0.71073$ Å) radiation. X-ray diffraction intensities were collected (ω scans with θ and κ-offsets), integrated and scaled with CrysAlisPro suite of programs. The unit cell parameters were obtained by least-squares refinement (based on the angular settings for all collected reflections with intensities larger than seven times the standard deviation of measurement errors) using CrysAlisPro. Data were corrected empirically for absorption employing the multi-scan method implemented in CrysAlisPro. The fac-[Re(CO)$_3$(bpy)(nHo)]CF$_3$SO$_3$ crystal was measured with an Enraf-Nonius Kappa-CCD diffractometer employing graphite-monochromated MoKα radiation. Diffraction data were collected (φ and ω scans with κ-offsets) with COLLECT.$^{31}$ Integration and scaling of the reflections was performed with HKL DENZO-SCALEPACK suite of programs. The unit cell parameters were obtained by least-squares refinement based on the angular settings for all collected reflections with intensities larger than seven times the standard deviation of measurement errors) using CrysAlisPro. Data were corrected numerically for absorption with PLATON$^{35}$ and also for extinction effects. The structures were solved by direct methods with SHELXS of the SHELX package$^{36}$ and the molecular model developed by alternated cycles of Fourier methods and full-matrix least-squares refinement with SHELXL of the same suit of

**X-ray diffraction data**

Single crystals suitable for X-ray diffraction analysis for both complexes were obtained by a slow evaporation from methanol/hexane solutions. The measurements of fac-[Re(CO)$_3$(phen)(nHo)]CF$_3$SO$_3$ crystal were performed on an Oxford Xcalibur, Eos, Gemini CCD diffractometer with graphite-monochromated MoKα ($\lambda = 0.71073$ Å) radiation. X-ray diffraction intensities were collected (ω scans with θ and κ-offsets), integrated and scaled with CrysAlisPro suite of programs. The unit cell parameters were obtained by least-squares refinement (based on the angular settings for all collected reflections with intensities larger than seven times the standard deviation of measurement errors) using CrysAlisPro. Data were corrected empirically for absorption employing the multi-scan method implemented in CrysAlisPro. The fac-[Re(CO)$_3$(bpy)(nHo)]CF$_3$SO$_3$ crystal was measured with an Enraf-Nonius Kappa-CCD diffractometer employing graphite-monochromated MoKα radiation. Diffraction data were collected (φ and ω scans with κ-offsets) with COLLECT.$^{31}$ Integration and scaling of the reflections was performed with HKL DENZO-SCALEPACK suite of programs. The unit cell parameters were obtained by least-squares refinement based on the angular settings for all collected reflections with intensities larger than seven times the standard deviation of measurement errors) using CrysAlisPro. Data were corrected numerically for absorption with PLATON$^{35}$ and also for extinction effects. The structures were solved by direct methods with SHELXS of the SHELX package$^{36}$ and the molecular model developed by alternated cycles of Fourier methods and full-matrix least-squares refinement with SHELXL of the same suit of

**Mass spectrometry analysis**

**HRESI-MS analysis.** High resolution electrospray ionization (HRESI) mass spectrometry (MS) analysis was performed in positive ion mode using the mass spectrometer BRUKER microTOF-Q II equipped with CID. Acquisition parameters: capillary temperature, 180 °C; nebulizer pressure, 0.4 Bar; capillary voltage, 4500 V; dry heater temperature, 200 °C; end plate offset voltage, −450 V; set dry gas at 4.0 l min$^{-1}$; collision cell RF, 150.0 Vpp. Stock solutions of the Re(i)-nHo complexes were prepared in methanol at a concentration 10$^{-4}$ M. When formic acid was added to the methanolic complex solutions the molecular ions were not detected. Diluted solutions were prepared from the stock solutions.

**MALDI-TOF/TOF MS analysis.** The Re(i)-nHo complexes were analyzed by ultraviolet matrix assisted laser desorption-ionization mass spectrometry (UV–MALDI MS) performed on the Bruker Daltonics Ultraflex II TOF/TOF mass spectrometer (Leipzig, Germany). Mass spectra were acquired in linear positive and negative ion modes and with the LIFT device in the MS/MS mode. Stock solutions of complexes (10$^{-4}$ M) were prepared in methanol. These solutions were then diluted 10 to 100-fold to a final concentrations 10$^{-5}$ to 10$^{-6}$ M. External mass calibration was made using β-cyclodextrin (MW 1134) with norharnane as matrix in positive and negative ion mode. The matrix signal was used as an additional standard for calibration in both ionization modes. Sample solutions were spotted on a MTP 384 polished stainless steel target plate from Bruker Daltonics (Leipzig, Germany). Matrix solutions were prepared by dissolving nHo (1 mg ml$^{-1}$) in acetonitrile/water (1 : 1, v/v) solution and DCTB$^{29,30}$ (10 mg ml$^{-1}$) in dichloromethane. For UV-MALDI MS experiments sandwich method was used according to Nonami et al.$^{31}$ i.e., loading successively 0.5 μl of matrix solution, analyte solution and matrix solution after drying each layer at normal atmosphere and room temperature. Desorption/ionization was obtained by using the frequency-tripled Nd:YAG laser (355 nm). Spectra were obtained and analyzed with the programs FlexControl and FlexAnalysis, respectively.
programs. The H-atoms of the organic ligand were positioned sterically and refined with the riding model. The fac-[Re(CO)3]phen(nHo)CF3SO3 crystal showed disordered solvent which could not be modeled satisfactorily in terms of the expected solvent molecules. Therefore, it was resorted to SQUEEZE17 procedure to eliminate from the diffraction data the contribution due to this disordered electron density followed by the refinement of the ordered part. In fac-[Re(CO)3bpy](nHo)]-CF3SO3 crystal the CF3SO3− counter-ion showed appreciable positional disorder and all but the carbon atom were treated anisotropically. Crystal data and structure refinement results for fac-[Re(CO)3][L](nHo)]CF3SO3 (L = bpy, phen) are in Table 1. Full crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (CCDC). Any request to the CCDC for this material should quote the full literature citation and the reference number CCDC 1038266 (phen) and CCDC 1038267 (bpy).

**Computational details**

DFT and TD-DFT calculations of ground and excited state properties of a series of Re(i) tricarbonyl complexes have been recently employed to interpret the experimental UV-vis absorption bands due to a set of MLCT, LLCT and IL transitions.38

The ligand nHo coordinated to Re by the pyridine N (N-2) may adopt different orientations, hence generating conformational isomers. These conformers only differ in the direction of the pyrrolic NH group (N-9). DFT calculations on the electronic structure of the complexes were carried out with Gaussian 09 software.39-42 Ground state geometry optimization was performed on two conformers of [Re(CO)3bpy](nHo)]+ (named hereafter Re-1 and Re-2, see Fig. 2) with the B3LYP hybrid functional using the LanL2DZ basis set.43-46

Vibration frequencies were computed at the same level of theory to confirm that these structures were minima on the energy surfaces. The cartesian coordinates corresponding to the X-ray structure were used as starting positions in the optimization process of the Re-1 structure. In this conformer the coordinated nHo molecule lies onto a plane bisecting both N-Re-C angles. On the other hand, in the Re-2 conformer, the coordinated nHo molecule is rotated 90° respect to its position.

### Table 1  Crystal data and structure refinement results for of fac-[Re(CO)3(L)(nHo)]CF3SO3 (L = phen, bpy) complexes

| Compound | L = phen | L = bpy |
|----------|----------|---------|
| Empirical formula | C27 H16 F3 N4 O6 Re S | C25 H16 F3 N4 O6 Re S |
| Formula weight | 767.70 | 743.68 |
| Temperature (K) | 295(2) | 295(2) |
| Wavelength (Å) | 0.71073 | 0.71073 |
| Crystal system | Monoclinic | Trigonal |
| Space group | P21/n | P31 |
| Unit cell dimensions | | |
| a (Å) | 11.7831(2) | 15.1660(9) |
| b (Å) | 13.8328(3) | 15.1660(9) |
| c (Å) | 17.5603(6) | 19.9800(7) |
| α (°) | 90.00 | 90.00 |
| β (°) | 94.139(3) | 90.00 |
| γ (°) | 90.00 | 90.00 |
| Volume (Å³) | 2854.75(9) | 1987.9(2) |
| Z, density (calculated, mg m⁻³) | 4, 1.786 | 4, 1.864 |
| Absorption coefficient (mm⁻¹) | 4.397 | 4.732 |
| f(000) | 1508 | 1080 |
| Crystal shape/color | Fragment/yellow | Fragment/yellow |
| Crystal size (mm³) | 0.331 x 0.194 x 0.183 | 0.211 x 0.066 x 0.059 |
| θ-range (°) for data collection | 295 to 27.00 | 295 to 25.99 |
| Index ranges | | |
| Reflections collected | 16412 | 10339 |
| Independent reflections | 6159 [R(int) = 0.0217] | 5145 [R(int) = 0.0624] |
| Observed reflections [I > 2σ(I)] | | |
| Completeness (%) | 99.0 (to θ = 27.00°) | 99.8 (to θ = 25.995°) |
| Absorption correction | Semi-empirical from equivalents | Numerical |
| Max. and min. transmission | | |
| Refinement method | Full-matrix least-squares on F² | Full-matrix least-squares on F² |
| Data/restraints/parameters | 6163/0/379 | 5145/1/357 |
| Goodness-of-fit on F² | 1.062 | 0.984 |
| Final R indices [I > 2σ(I)] | R₁ = 0.0305, wR₂ = 0.0773 | R₁ = 0.0537, wR₂ = 0.1390 |
| R indices (all data) | R₁ = 0.0441, wR₂ = 0.0833 | R₁ = 0.0648, wR₂ = 0.1457 |
| Extinction coefficient | | |
| Absolute structure parameter | | |
| Largest diff. peak and hole (e Å⁻³) | 1.686 and −0.574 | 0.029(2) and −0.02(2) |

ₐ R₁ = \(\sum |F_o| - |F_c| / \sum |F_o|\), wR₂ = \(\sum w(|F_o|² - |F_c|²)²/\sum w|F_o|²)²/².
in the Re-1 conformer, bisecting now the N-Re-N and C-Re-C angles. The energies of the vertical electronic transitions were computed at the optimized geometry of the ground-state by TD-DFT. The number of calculated singlet-to-singlet electronic transitions was 110. Both optimized geometries and TD-DFT calculations were carried out including solvent (MeOH) effects through the Polarizable Continuum Model (PCM). The energies of the vertical electronic transitions were 110. Both optimized geometries and TD-DFT calculations were carried out including solvent (MeOH) effects through the Polarizable Continuum Model (PCM).50 Output files from Gaussian 09 were analyzed with the AOMix program to obtain the percentage compositions of different molecular fragments to molecular orbitals (MOs). GaussSum 2.2.5 program was used to simulate absorption spectra with Gaussian distributions with a full-width at half-maximum (fwhm) set to 3000 cm⁻¹.

Results and discussion

Spectroscopic characterization

The [Re(CO)₃(L)(nHo)]CF₃SO₃ (L = bpy or phen) complexes were obtained in good yields and fully characterized by elemental analysis, FTIR and NMR spectroscopy (¹H and ¹³C), MALDI and HRESI mass spectrometry.

Structural X-ray diffraction methods were used on single crystals obtained for both complexes. The FTIR absorption spectra of the complexes are consistent with both the facial configuration of the carbonyl ligands and with their C₈ symmetry, as revealed by the presence of two intense absorption bands in the 2100–1800 cm⁻¹ region. According to previous reports on similar compounds, the sharp band at higher frequency (ca. 2031 and 2030 cm⁻¹ to L = bpy and phen, respectively) is attributed to the A’1 mode (the in-phase totally symmetric stretch of the three CO ligands). The spectra show other broad band (ca. 1920 and 1915 cm⁻¹ to L = bpy and phen, respectively) which can be assigned to the A’2 (totally symmetric out-of-phase stretching) and A’ modes (asymmetric stretching of the equatorial carbonyls ligands). In fact, A’2 and A’ bands have already been observed as bands superimposed into a single broad band in fac-[Re(CO)₃(NN)(R-pyridyl)]⁺ complexes, where the environment of Re is more symmetric (Re bound to three CO and three pyridinic nitrogen) than other Re (i) tricarbonyl complexes (e.g. fac-[Re(CO)₃(NN)(L)], L = halide, CF₃SO₃⁻, etc.). The patterns observed in the obtained complexes are in agreement with the high symmetry expected around the metal center due to the coordination of nHo ligand by pyridine N (N-2) as shown by the X-ray results (see below).

Compared to the free norharneman ligand, the FTIR spectra of the complexes showed slight shift to higher frequencies in the region 1200–1700 cm⁻¹ (Δν < 10 cm⁻¹). Most remarkable differences were observed on N–H peak of nHo ligand in the complexes (N9–H). While N–H peak of free nHo is observed at 3419 cm⁻¹ the complexes showed significant shifts to lower frequencies (3257 and 3260 cm⁻¹ to bpy and phen, respectively) These shifts are typical features that indicate that norharneman is coordinated to the metal core in a similar way to that reported recently for Ag(i)–nHo complexes.57

HRESI-MS and UV-MALDI-MS

Mass spectrometry was used to study the molecular structure of rhenium complexes. Fig. S1† shows the HRESI mass spectrum in positive ion mode of the complex [Re(CO)₃(bpy)(nHo)]⁺ CF₃SO₃. The intact cationic moiety belonging to the molecular ion, [Re(CO)₃(bpy)(nHo)]⁺, as [M⁺] at m/z = 595.08, the fragment formed when a CO ligand is lost [M – (CO)]⁺ at m/z = 566.88 and the one formed when nHo ligand is lost [M – (nHo)]⁺ at m/z = 427.00 were observed. Additionally, a signal at m/z = 169.08 was detected, corresponding to nHo ligand. As mentioned by Wyatt in a recent review,29 ESI-MS has been more used for the analysis of organometallic complexes than UV-MALDI-MS, however there are instances when both techniques may be used in a complementary fashion. Furthermore, it is necessary to expand previous studies of organometallic compounds using UV-MALDI-MS to obtain information of new compounds that could act as efficient matrices. Since [Re(CO)₃(bpy)(nHo)]CF₃SO₃ complex shows strong absorption in the UV-vis region (see below), particularly at 355 nm, laser desorption ionization mass spectrometry (LDI-MS), without needing the presence of a secondary molecule as photosensitizer or matrix in the sample, was used. It is worth noticing that previously nHo has been used as MALDI matrix for the detection of organometallic compounds.30 As shown in Fig. S1† intact cation moiety of the molecular ion of this complex could be detected in positive ion mode but the signal obtained was very weak. Additionally, two more structure diagnosis signals were obtained when comparing with the ESI spectrum described before, [M – 3(CO)]⁺ at m/z = 511.16 and [M – (CO) – (nHo)]⁺ m/z = 399.06. MALDI mass spectra of [Re(CO)₃(bpy)(nHo)]CF₃SO₃ complex were recorded using DCTB and nHo as matrices. Both matrices have been previously used for analysis of rhenium complexes.30,58 Fig. S1† shows the spectrum recorded using DCTB as matrix. Similar results were obtained when nHo was used (result not shown). Some fragments produced by the loss of one or more ligands were observed using both techniques but as UV-MALDI-MS is a softer ionization technique than LDI-MS it was possible to detect the intact molecular ion of the complex under study with better signal-to-noise ratio. All ionization methods used allowed to detect the intact molecular ion. However, the total intensity for signal at m/z = 595.08 was higher when ESI was used instead of MALDI.
Fig. S2 shows ESI mass spectrum in positive ion mode of the complex [Re(CO)₃(phen)(nHo)]CF₃SO₃. The intact cation moiety of the molecular ion was detected as [M]+ at m/z = 619.07 together with the one formed when nHo ligand is lost [M – (nHo)]+ at m/z = 451.00. LDI and MALDI mass spectra showed similar signals. The intact cation moiety of the molecular ion was detected with better signal-to-noise ratio in MALDI compared with LDI experiment. Additionally, the fragments formed when one or more CO and/or nHo ligands were lost, [M – (CO)]+ at m/z = 591.17, [M – 3(CO)]+ at m/z = 535.17, [M – (nHo)]+ at m/z = 451.08 and [M – (CO)(nHo)]+ at m/z = 423, were respectively observed. Table S2a and S2b† show the most representative ions related to the Re(nHo) complexes observed with the different ionization methods used in this work. Finally, it is interesting to mention that when formic acid was added to the methanolic complex solutions used in the ESI-MS experiments, the molecular ions were not detected in agreement with the fact that the protonated nHo pyridine N yielded in the presence of formic acid is the same nHo pyridine N involved in the Re–nHo linkage, which is destroyed in acidic medium.

Structural characterization

Fig. 3 and 4 are ORTEP plots of solid state fac-[Re(CO)₃(L)(nHo)]CF₃SO₃ (L = phen, bpy) showing that both complexes are structurally closely related to each other by interchange of the phenanthroline and bipyridine bidentate ligands. Intra-molecular bond distances and angles around the metal are compared in Table 2. We shall discuss the structure of the better refined phenanthroline-containing complex.

Rhenium(1) ion is in a slightly distorted octahedral environment, cis-coordinated to three carbonyl (CO) groups [Re–C distance in the range from 1.919(6) to 1.930(4) Å].

The isotropic atomic displacement parameter for the disordered CF₃SO₃ counter-ion has been arbitrarily set to 0.05 Å².

![Fig. 3](file:///C:/Users/username/Desktop/Figure3.png)

**Fig. 3** View of fac-[Re(CO)₃(phen)(nHo)]CF₃SO₃ showing the labeling of the non-H atoms and their displacement ellipsoids at the 30% probability level. Metal–ligand bonds are indicated by open lines and the intermolecular H-bond by dashed lines.

![Fig. 4](file:///C:/Users/username/Desktop/Figure4.png)

**Fig. 4** View of fac-[Re(CO)₃(bpy)(nHo)]CF₃SO₃ in the solid. The isotropic atomic displacement parameter for the disordered CF₃SO₃ counter-ion has been arbitrarily set to 0.05 Å².

- **Table 2** Bond lengths [Å] and angles [°] around rhenium ion for fac-[Re(CO)₃(L)(nHo)]CF₃SO₃ (L = phen, bpy) complexes

| L: phen | L: bpy |
|--------|--------|
| Re–C(1) | 1.919(6) Re–C(1) | 1.93(3) |
| Re–C(2) | 1.930(4) Re–C(2) | 1.84(2) |
| Re–C(3) | 1.923(5) Re–C(3) | 1.93(3) |
| Re–N(1) | 2.187(3) Re–N(11) | 2.20(2) |
| Re–N(12) | 2.176(4) Re–N(12) | 2.19(2) |
| Re–N(21) | 2.207(3) Re–N(21) | 2.23(2) |

| C–Re–C | 89.6(2) C–Re–C | 88.2(9) |
| C–Re–C | 87.9(2) C–Re–C | 88.2(8) |
| C–Re–C | 86.3(2) C–Re–C | 84.7(9) |
| C–Re–C | 91.5(2) C–Re–C | 93.6(7) |
| C–Re–C | 173.5(1) C–Re–C | 175.0(8) |
| C–Re–C | 100.2(2) C–Re–C | 99.9(7) |
| C–Re–C | 97.1(2) C–Re–C | 94.3(7) |
| C–Re–C | 97.8(2) C–Re–C | 100.2(8) |
| C–Re–C | 173.6(2) C–Re–C | 174.5(7) |
| C–Re–C | 73.7(1) C–Re–C | 75.3(6) |
| C–Re–C | 173.1(2) C–Re–C | 178.1(7) |
| C–Re–C | 96.8(2) C–Re–C | 93.5(7) |
| C–Re–C | 90.0(2) C–Re–C | 92.6(7) |
| C–Re–C | 82.4(1) C–Re–C | 84.6(6) |
| C–Re–C | 84.6(1) C–Re–C | 84.7(6) |
UV-vis absorption spectroscopy

The UV-vis absorption spectra of [Re(CO)₃(L)(nHo)]CF₃SO₃ complexes in MeOH solutions (Fig. 5) present similar features and thus they will be discussed together. They consist of three different groups of absorption bands. In the first group appear the most intense bands (ε ~ 4-4.5 × 10⁴ M⁻¹ cm⁻¹). For [Re(CO)₃(bpy)(nHo)]⁺ these bands are centered at λ₂₅₄ = 241 and 249 nm and a shoulder appears at 261 nm. For [Re(CO)₃(phen)(nHo)]⁺ the position of the most intense bands are somewhat red-shifted with λ₂₅₄ = 252 nm and a shoulder at 273 nm. The second group is less intense than those of the first group (ε ~ 2.5–3 × 10⁴ M⁻¹ cm⁻¹): peaks at λ₃₀₁ = 306 nm with a shoulder at 319 nm for [Re(CO)₃(bpy)(nHo)]⁺ and λ₃₀₁ = 301 nm for [Re(CO)₃(phen)(nHo)]⁺ respectively. The weakest bands (ε ~ 8–9 × 10³ M⁻¹ cm⁻¹) are observed between 320 and 450 nm, i.e., for [Re(CO)₃(phen)(nHo)]⁺ one band peaking at λ₃₅₅ = 355 nm with a shoulder at 368 nm are observed. Those bands are nearly identical for [Re(CO)₃(phen)(nHo)]⁺ complex, both in position and intensity. For both complexes, a long tail extending from 400 to 450 nm indicates the existence of at least one other absorption band with λₙₐₓ in the 370–400 nm interval. For comparative purposes, Fig. 5 also shows the absorption spectrum of nHo in methanolic solution with HClO₄ (nHo in the protonated form, nHoH⁺). Additionally, electronic absorption data were summarized in Table 3 in order to facilitate the comparison.

The UV-vis absorption spectra of both [Re(CO)₃(bpy)(nHo)]⁺, [Re(CO)₃(phen)(nHo)]⁺, [Re(CO)₃(bpy)(nHo)]⁻, and [Re(CO)₃(phen)(nHo)]⁻ complexes showed significant spectroscopic differences respect to the sum of the nHoH⁺ and [Re(CO)₃(L)]⁻ electronic absorption spectra. Those new spectral features were used to identify the coordination of nHo ligand during the reaction. In particular, the new band that arises at λ ~ 305 nm in the absorption spectra of both complexes is not present in the absorption spectra of the precursors. On the other hand, this band shows features similar to the ones observed in the spectrum of protonated norharmane, suggesting mono-dentate coordination to the metal core by the pyridine N-atom. In addition, the absorptions observed between 350–450 nm suggests also new charge transfer transitions bands by coordination of nHo. In order to get a deeper understanding of the absorption spectrum of [Re(CO)₃(L)(nHo)]CF₃SO₃ complexes, in terms of a set of MLCT, LLCT and IL electronic transitions, DFT and TD-DFT calculations were performed for the [Re(CO)₃(bpy)(nHo)]⁺ complex and the results are presented in the next sections.

Quantum chemistry of [Re(CO)₃(bpy)(nHo)]⁺

DFT calculations. Ground state geometry optimization results on two Re-1 and Re-2 conformers of [Re(CO)₃(bpy)(nHo)]⁺, Fig. 2, provide additional structural information. The accuracy of these calculations were monitored by comparing them with the corresponding X-ray crystallographic data obtained for Re(i) tricarbonyl complex. The theoretical values for selected bond distances and angles for Re-1 and Re-2 are shown in Table 4. They are in good agreement with those obtained by X-ray diffraction, with bond lengths differing in less than 0.1–0.2 Å and bond angles by 3° or less. From the comparison of the sum of electronic energy plus zero point energy for both conformers it is concluded that Re-1 is more stable than Re-2 in about 0.8 Kcal mol⁻¹. Though intermediate conformations of [Re(CO)₃(bpy)(nHo)]⁺ with different angles of the nHo ligand between those in Re-1 and Re-2 conformers were not examined, it is highly probable that in fluid solution the ligand nHo molecule may rotate freely (remember also that kT ~ 0.6 Kcal mol⁻¹ at 298 K).

To interpret the nature of the experimental UV-vis absorption bands, TD-DFT calculations were performed on the opti-

Table 3

| Complex                | λ₁ (nm) | ε₁ | λ₂ (nm) | ε₂ | λ₃ (nm) | ε₃ |
|------------------------|--------|----|--------|----|--------|----|
| [Re(CO)₃(bpy)(nHo)]⁻   | 368    | 6.9| 355    | 6.7| 351    | 6.7|
| [Re(CO)₃(phen)(nHo)]⁻ | 369    | 6.9| 355    | 6.7| 351    | 6.7|
| nHoH⁺                  | 371    | 4.3| 301    | 23.7| 248    | 27.3|
| [Re(CO)₃(bpy)(nHo)]⁺   | 368    | 5.9| 355    | 6.7| 301    | 15.0|
| [Re(CO)₃(phen)(nHo)]⁺  | 369    | 5.9| 355    | 6.7| 301    | 15.0|

Fig. 5 UV-vis absorption spectra of [Re(CO)₃(bpy)(nHo)]CF₃SO₃ (red), [Re(CO)₃(phen)(nHo)]CF₃SO₃ (black) in MeOH, and nHoH⁺ (blue, nHo in MeOH + HClO₄).
mized structures of Re-1 and Re-2 conformers at the B3LYP/LanL2DZ/PCM level of theory. The TD-DFT results are summarized in Table S3† where they are compared with the corresponding experimental data. The MOs which are mainly responsible for the electronic transitions observed in the absorption spectrum of the Re(I) complex within the 220–500 nm wavelength range are: HOMO, LUMO, and the groups of MOs H−8 through H−1 and L+1 through L+7. The percentage compositions of those MOs were obtained from Mulliken population analysis with the aid of AOMIX program from contributions of four fragments, namely: (i) Re atom, (ii) the three carbonyls, (iii) bpy molecule and (iv) nHo molecule. Fig. 6 and 7 show the spatial plots of a selection of those MOs most representative in Re-1 and Re-2 conformers, respectively. Tables S4 and S5† show the calculated % compositions of all fragments at each MO for Re-1 and Re-2 along with % composition vs. Energy plots.

We give below a brief description of relevant MOs of Re-1 in terms of the fragments percentage compositions. H and H−6 are bonding MOs almost exclusively composed (>99% character) of nHo molecule π-orbitals.

In H−1 the charge density distribution is mainly concentrated on nHo (54%), Re (29%) and COs (13%), with a very small contribution of bpy (3%) to that MO. H−5 and H−7 are bonding MOs of π character exclusively centered on bpy (>95% character). H−3 and H−4 are bonding MOs mainly centered on the Re atom (54% and 45% character, respectively) with smaller contributions of COs and nHo (between 20 and 30%) and even smaller (~4%) contributions of bpy orbitals. H−2 consists mainly in Re (63%) and COs (28%) orbitals. LUMO, L+2 and L+3 are anti-bonding orbitals exclusively centered on bpy fragment. L+1 is an anti-bonding MO nearly exclusively centered on nHo fragment (87% composition) with a smaller participation of bpy (8%) and COs (4%) fragments. L+4 and L+5 are antibonding MOs mainly centered on the COs fragments (75%) with around 20% contribution of Re atom. L+6 is an antibonding MO mainly centered on nHo fragment (67%) with 28% of contribution from COs. L+7, on the other hand, is an antibonding MO mainly centered on COs fragments (70%) with 27% of contribution from nHo. MOs orbitals of Re-2 are very similar in nature to those of Re-1. The only significant difference arises in H−3 of Re-2: a bonding MO mainly centered on the nHo fragment (58%) with around 26% contribution of Re atom, 11% of COs and 5% of bpy.

Since the simulated absorption spectrum derived from TD-DFT calculations on Re-2 gave much better agreement (see below) than that of Re-1 when compared with experimental data for [Re(CO)₃(bpy)(nHo)]⁺ in MeOH, only TD-DFT calculated electronic transitions of Re-2 will be discussed in detail. However, the most significant differences between TD-DFT calculated electronic transitions of Re-2 and Re-1 will be highlighted later below. In general, for Re-2 it is observed that the main spectral features are predicted by TD-DFT calculations with good accuracy, both in position and relative intensities.
In the 220–300 nm wavelength region, the two observed high intensity bands centered at $\lambda_{\text{max}} = 241$ and 249 nm (the latter with a shoulder at 261 nm) are predicted by TD-DFT as a set of five electronic transitions (see Table S3b,† yellow highlighted). $\text{H}_{-5} \rightarrow \text{L}+2$ and $\text{H}_{-6} \rightarrow \text{L}+1$ are $\pi \rightarrow \pi^*$ electronic transitions centered in bpy and nHo fragments, respectively. The most intense electronic transitions are $\text{H}_{-3} \rightarrow \text{L}+6$ and $\text{H}_{-2} \rightarrow \text{L}+7$, which are LLCTnHo$\rightarrow$COs electronic transitions. $\text{H}_{-4} \rightarrow \text{L}+4$ is an admixture of LLCTnHo$\rightarrow$COs and MLCTRe$\rightarrow$COs electronic transitions. The spectral features observed in the absorption spectrum of $[\text{Re(CO)}_3(\text{bpy})(\text{nHo})]^+$ between 300 and 320 nm (a medium intensity band centered at $\lambda_{\text{max}} = 306$ nm with a shoulder at 319 nm) are predicted by TD-DFT as a series of four electronic transitions (see Table S3b,† green highlighted). The most intense, i.e. $\text{H}_{-1} \rightarrow \text{L}+1$, is a LLCTnHo$\rightarrow$COs electronic transition. $\text{H}_{-4} \rightarrow \text{L}+1$ is also a LLCTnHo$\rightarrow$COs electronic transition. $\text{H}_{-5} \rightarrow \text{L}$ is a $\pi \rightarrow \pi^*$ electronic transition centered on bpy. $\text{H}_{-1} \rightarrow \text{L}+3$ is an admixture of a MLCTRe(CO)$_3$$\rightarrow$bpy and a LLCTnHo$\rightarrow$bpy electronic transitions. Finally, in the lowest energy region, the observed absorption band at $\lambda_{\text{max}} = 355$ nm with a shoulder at 368 nm are predicted by TD-DFT as two electronic transitions (see Table S3b,† grey highlighted). $\text{H}_{-1} \rightarrow \text{L}+1$ is mainly a $\pi \rightarrow \pi^*$ electronic transition of nHo. $\text{H}_{-4} \rightarrow \text{L}$, however, is a MLCTRe(CO)$_3$$\rightarrow$bpy electronic transition. The calculated electronic spectra of $[\text{Re(CO)}_3(\text{bpy})(\text{nHo})]^+$ is simulated from the theoretical results to ease the comparison with experimental data. The simulations are shown in Fig. 8 in comparison with the experimental absorptions. It is observed that the simulated spectrum for Re-2 compares very well with the experimental one.

The comparison of the experiments with the simulated spectrum for Re-1 is not so good since Re-1 spectrum fails to reproduce the experimental absorption spectrum in the 350–400 nm wavelength region and reproduces poorly the bands at $\lambda_{\text{max}} = 306$ nm and the shoulder at 319 nm. However, Re-1 spectrum reproduces quite well the high energy bands and it also gives a good account of the observed long tail spreading between 400 and 450 nm. Since, as noted above, both conformers differ in the sum of electronic plus zero point energies in a small energy amount, in fluid solutions there may be a rapid interchange between many possible conformations and thus the observed absorption spectrum could be a time-averaging of all of them. The main difference between Re-1 and Re-2 TD-DFT calculations appears in the 300–450 nm wavelength region. $\text{H}_{-1} \rightarrow \text{L}$ is the only calculated electronic transition with significant intensity in the lowest energy region, which corresponds to an admixture of MLCTRe(CO)$_3$$\rightarrow$bpy and a LLCTnHo$\rightarrow$bpy electronic transitions (see Table S3a,† yellow highlighted). In the 300–325 nm spectral region, both

Fig. 7 Spatial plots of most representative MOs in Re-2 conformer.

![Fig. 7](image_url)

Fig. 8 Comparison of the UV–vis absorption spectrum (black curves) with TD-DFT calculated electronic transitions (blue lines) and simulated spectra (red curves) for (a) Re-2/PCM/MeOH and (b) Re-1/PCM/MeOH conformers.

![Fig. 8](image_url)
confirmed the more stable structure of
by X-ray diffraction in the solid state confirmed the monocarboxylic coordination of nHo and also showed the three carboxyls in face coordination. The octahedral coordination around the central metal is completed by a bidentate L ligand (L = bpy or phen). Structural analysis was deepened by the comparative use of a two mass spectrometry techniques, HRESI and MALDI–MS. Ground state geometry optimization confirmed the more stable structure of [fac–Re(CO)₃(bpy)(nHo)]⁻ and theoretical spectrum of Re-2 when compared with that of Re-1.

Conclusions
Two new norharmane Re(i) complexes, Re(i)–nHo, have been obtained successfully. As far as we know this is a beginning of a new family of Re(i) coordination compounds including a β-carboline as a ligands. Coordination of nHo to Re(i) through pyridine N-atom in solution was evidenced by different spectroscopic techniques. Structural characterization by X-ray diffraction in the solid state confirmed the monocarboxylic coordination of nHo and also showed the three carboxyls in face coordination. The octahedral coordination around the central metal is completed by a bidentate L ligand (L = bpy or phen). Structural analysis was deepened by the comparative use of a two mass spectrometry techniques, HRESI and MALDI–MS. Ground state geometry optimization confirmed the more stable structure of [fac–Re(CO)₃(bpy)(nHo)]⁻ and theoretical spectrum of Re-2 when compared with that of Re-1.

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