Kinetics and photophysical behavior of the P,N-ReI complex [P,N-{(C₆H₅)₂(C₅H₄N)P}Re(CO)₃(O₃SCF₃)]: A directly coordinated (and labile) triflate

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The reaction of [P,N-{(C₆H₅)₂(C₅H₄N)P}Re(CO)₃Br] (RePNBr) with silver triflate leads to the complex [P,N-{(C₆H₅)₂(C₅H₄N)P}Re(CO)₃(O₃SCF₃)] (RePNTfO) with moderate yield. This new P,N-ReI triflate compound contains the anion directly coordinated to the metal, completing an octahedral environment. RePNTfO displays in dichloromethane (DCM) solution an irreversible oxidation about +1.35 V and three irreversible reduction processes at −1.38 V, −2.03 V and −2.30 V. Oxidation has been attributed to the Re⁠/ReII couple, while the reduction corresponds to P₄N-ligand processes, which is consistent with those computed by means of DFT. The absorption spectrum of RePNTfO in DCM displays a maximum at 295 nm (ε = 7.1 × 10³ M⁻¹ cm⁻¹) and a shoulder around 350 nm (ε = 1.8 × 10³ M⁻¹ cm⁻¹), which have been assigned to intraligand (π → π⁺) and metal to ligand charge transfer (MLCT, d → π⁺) transitions with the help of DFT/TDDFT. Excitation of RePNTfO in DCM at 350 nm leads to an emission spectrum centered at 535 nm. The analysis of the variation of the absorption and emission spectra in coordinating solvents compared to non-coordinating DCM, DFT/TDDFT calculations modeling and ELF analysis suggest for coordinating solvents that triflate ligand is replaced in the coordination sphere of ReI in solution. Kinetics of the exchange of triflate by bromide measured in DCM at different temperatures allowed to estimate the Eyring parameters: ΔH°, ΔS° and ΔG°, 50.8 kJ mol⁻¹, −109.6 J K⁻¹ mol⁻¹ and 83.5 kJ mol⁻¹ respectively. The high negative entropy is indicative of a compact transition state, compatible with an associative mechanism, Iₙ, for the exchange.

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1. Introduction

Mononuclear ReI tri-carbonyl complexes having a chelating P,N-molecule have been considerably less studied than the corresponding N,N-diimines. The presence of a phosphorous atom in the chelating ligand opens new possibilities, due to its trans-effect (and labile) triflate

Mononuclear ReI tri-carbonyl complexes having a chelating P,N-molecule have been considerably less studied than the corresponding N,N-diimines. The presence of a phosphorous atom in the chelating ligand opens new possibilities, due to its trans-effect (and labile) triflate
Briefly, to a solution of 800.8 mg of \([P\cdot N\cdot(C_{6}H_{5})_{2}(C_{6}H_{4}N)P] Re(CO)_{3}Br\) (RePNBr) (1.305 mmol) in toluene (75 mL) was added to a solution of 335.2 mg of silver triflate (1.305 mmol) in toluene (50 mL), and stirred at room temperature, isolated from light, during 2 h. After reaction, the resulting silver bromide was filtered off. Addition of pentane to this solution leads to precipitation of the complex, allowing the isolation of 492.9 mg of crude RePNTfO (55.4% yield). Recrystallization by slow diffusion of pentane to a toluene solution of RePNTfO leads to almost transparent and very slightly amber crystals of the compound, which were found suitable for further structural analysis.

**Elemental Analysis:** Calculated (experimental) for \(C_{21}H_{14}F_{2}N_{4}O_{3}P_{2}Re\): C: 36.65% (37.10); H: 2.07% (2.24); N: 2.05% (2.21); S: 4.70% (5.33). FITR-ATR (major peaks cm\(^{-1}\)):

- C=C–O: 2035, 1912, 1900. 0.93 Å. Uiso(H) values were set equal to 1.2 Ueq of the parent carbon.

**2.2. Structural determination**

The crystal structure of RePNTfO at 293 K was determined by X-ray diffraction on a stick-shaped 0.10 mm \(\times\) 0.05 mm \(\times\) 0.05 mm very slightly amber transparent crystal. Data collection was done on a SMART-APX II CCD diffractometer system. Data was reduced using S A N T [28], while the structure was solved by direct methods, completed by Difference Fourier Synthesis and refined by least-squares using S H E L X L [29]. The 

**2.3. Cyclic voltammetry**

Cyclic voltammetry studies were performed on a CH-Instruments 650E potentiostat. Cyclic voltammogram at 100 mV s\(^{-1}\) at room temperature was recorded in DCM (SeccoSolv\(^{\oplus}\) grade, Merck) solutions (1.0 mM) using tetrabutylammonium perchlorate \((n\text{-Bu}_{4}N\text{ClO}_{4})\) as the supporting electrolyte \((0.1 \text{ M})\). A standard three-electrode cell was used, with a 3-mm diameter glassy carbon (GC) working electrode, a platinum wire counter electrode, and an Ag/AgCl coupled with a Luggin capillary reference electrode. All potentials were referred to the redox potential of ferrocene \((F_{c})\)/ferrocerium ion \((F^{+})\) as an internal standard.

**2.4. Spectroscopic and photophysical measurements**

IR spectrum (4000–400 cm\(^{-1}\)) of the compound was measured using a Jasco FTIR-4600 spectrophotometer equipped with an ATR PRO ONE. \(^{1}H\) NMR spectrum was recorded on a Bruker Avance 400 MHz spectrometer at 298 K and using CDCl\(_{3}\) as solvent. UV–Vis spectra were recorded on an Agilent 8453 Diode-Array spectrophotometer in the range of 250–700 nm in aerated solvent solutions at room temperature. Emission spectra were measured in a Horiba Jobin-Yvon FluoroMax-4 spectrofluorometer in different solvents at room temperature or in ethanol–methanol glass (4:1, \(v/v\)) at 77 K. Luminescence lifetime measurements were carried out with the time correlated single photon counting technique using a Pico-Quant FluoroTime300 fluorescence lifetime spectrometer. A sub-nanosecond Pulsed LED PLS-280 or PLS-300 were employed as pulsed light sources (FWHM ~500 ps; average power 1 \(\mu\)W). Time resolved experiments were made in DCM solutions either air-equilibrated or argon-saturated. Emission quantum yields \((\Phi_{em})\) were measured using procedures described in literature using Quinine...
Sulphate in 0.1 M H$_2$SO$_4$ or [Ru(bpy)$_3$][(PF$_6$)$_2$] in acetonitrile solution as standard compounds [32,33]. Singlet oxygen, O$_2$(^1A$_g$), measurements were carried out in a Fluotime 200 consisting in a multichannel scaler Nanoharp 200. Excitation at 355 nm was achieved with a laser FTSS355-Q5, (Crystal Laser, Berlin, Germany) working at 1 kHz repetition rate. For the detection at 1270 nm a NIR PMT H10330A (Hamamatsu) was employed. The O$_2$(^1A$_g$) quantum yields (Φ$_{A_0}$) were determined by comparing the intensity at zero time of the 1270 nm signals to those of optically-matched solutions of phenalenone as Ref. [34]

2.5. Kinetics and thermodynamic parameters of ligand exchange process

All ligand exchange experiments conducted at different temperature considered the exchange reaction proposed in Scheme 3:

Under conditions [Br$^-$] >> [RePNTO], the observed rate constant, $k_{obs}$, was assumed to be equal to Eq. (1), where $k_0$ can be the contribution of an additional pre-dissociative process: [35,36]

$$k_{obs} = k_1[Br^-] + k_0$$  \hspace{1cm} (1)

Following the $k_{obs}$ dependence on the [Br$^-$], the second order rate constant, $k_1$, was determined at different temperatures. Using the Eyring Eq. (2):

$$\ln \left( \frac{k_1}{T} \right) = \ln \left( \frac{k_0}{T} \right) + \frac{\Delta S^*}{R} - \frac{\Delta H^*}{R} - \frac{1}{T}$$

the activation parameters $\Delta S^*$, $\Delta H^*$, and $\Delta G^*$ were determined.

2.6. Topological analysis of the electron localization function (ELF)

In order to gain a deeper insight concerning the nature of electron delocalization and bonding in this system, we resort to exploration of the topological analysis of the electron localization function $\eta(r)$ (ELF) [37,38]. The analysis of the gradient vector field of $\eta(r)$ leads directly to a unique division of the molecular space into basins of attractors related to the chemical concepts of structures and bonding. Within such a framework the basins are empirically associated to chemically meaningful concepts such as atomic cores and valence bonding and lone pairs regions. ELF can be interpreted in terms of the relative local excess of kinetic energy density associated to the Pauli principle. ELF is conveniently defined to be ranged in the [0,1] interval, where the highest values correspond to the spatial positions with high relative electron localization. Valence basin densities are naturally delocalized among those associated with the inner atomic shell densities of the core basins. Hence, it is expected that ELF analysis helps to unravel the nature of chemical bonding around the Re center. It should be emphasized however that the ELF electronic basin populations characterize only the spatial organization (not energetically aspects) of the bonding in terms of the electron pair localization [39–41].

2.7. Computational details

All geometry optimizations were performed at the B3LYP/6-31+G(d,p) level of theory using the Gaussian09 Rev C.01 package of programs (G09) [42], and started from geometry determined by means of X-rays diffraction. The LANL2DZ basis set was used only for Rhenium. Excited state calculations were performed within the time-dependent DFT methodology as implemented in G09. Solvent effect for simulating dichloromethane have been incorporated through the polarizable continuum model (PCM) using the integral equation formalism variant (IEFPCM) [43,44]. Absorption and emission spectra were simulated from the above calculations using the GaussSum 3.0 suite of freely available processing tools. A full width at half-maximum (FWHM) of the Gaussian curves corresponding to 3000 cm$^{-1}$ was employed to convolute both spectra. Representations for molecular orbitals were generated using the G09 cubegen tool and have been visualized using VMD and Povray 3.6 programs [45,46]. Topological analyses of $\rho(r)$ and $\eta(r)$ were performed using the TopMod [47] and Multiwfn [48] suite of packages.

3. Results and discussions

3.1. Structural description

The structure of the RePNTO complex is closely related to those of the parent RePNBr [11], and can be described as a central Re$^2$ ion octahedrally surrounded by three carbonyl groups in a fac-correlation, a chelating and bidentate pyridyl-diphenyl-phosphine (PN) molecule and a O-coordinated and monodentate triflate, as shown in Fig. 1. The N–Re–P bite angle, 65.67(12)$^\circ$, is a little bit closer to the value for a regular octahedron (90$^\circ$) compared to those described for the precursor RePNBr, 64.9(1)$^\circ$ [11]. The rhenium to the triflate anion oxygen atoms distances are 2.208(4) Å, 4.235 (6) Å and 3.652(5) Å for O4, O5 and O6 respectively, suggesting the triflate is firmly mono-coordinated to the rhenium atom. Table 1 shows the most significant bond distances and angles. A summary of the most relevant intermolecular interactions is given in Table S2.

3.2. Electrochemistry

Electrochemical properties of RePNTO have been studied by cyclic voltammetry (Fig. 2) and Square-Wave voltammetry (Fig. S2) using DCM and (N(n-Bu)$_4$)$(ClO$_4$)$_2$ as the supporting electrolyte. All measurements were referred to $F$/F$_c$ potential. The RePNTO complex presents an irreversible peak at around

$$\text{RePNTO} + \text{Br}^- \rightarrow \text{RePNBr} + \text{TFO}^-$$

Scheme 3. General reaction for the displacement of triflate by bromide ligand.

Fig. 1. Molecular structure diagram for RePNTO showing partial atom numbering scheme. Displacement ellipsoids drawn at the 50% level of probability. Hydrogen atoms are drawn as spheres of arbitrary radii.
+1.35 V, which has been attributed to ReI/ReII oxidation, as previously reported for ReNN, ReNNN [49] and RePNNBr [12] systems.

Furthermore, the system presents three irreversible reduction processes, with peaks ca. at /C0 1.38 V, /C0 2.03 V and /C0 2.30 V, which may be assigned to the stepwise reduction and decomposition of the organic ligand. It has been reported in literature for organometallic complexes containing the diphenyl-2-pyridylphosphine ligand in the structure, that these systems show three irreversible reduction processes at negative potentials [50]. Square-wave voltammetry experiments allowed to visualize and more clearly assign the different oxidation and reduction processes present in the system RePNTfO.

By comparison to RePNBr and related compounds [13], the last band has been assigned to a ligand reduction. To confirm this proposal, we have optimized the molecular structure of RePNTfO by means of DFT calculations. The computed structure in the gas phase closely resembles that determined by X-rays diffraction (Table S3). Vertical oxidation and reduction of the ReI molecule leads to odd-electron species, where the unpaired electron mainly resides on the rhenium atom in the oxidized specie RePNTfO+ (Fig. 3a) and into the ligand in the reduced specie RePNTfO− (Fig. 3b).

It is interesting to note that upon electron removal or addition, important distortions of the geometry of the corresponding species occur after optimization (Table S3), which is consistent with the observed irreversibility of both waves.

### Table 1

<table>
<thead>
<tr>
<th>Re1–C1</th>
<th>1.901(8)</th>
<th>Re1–N1</th>
<th>2.183(5)</th>
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<tbody>
<tr>
<td>Re1–C2</td>
<td>1.920(7)</td>
<td>Re1–O4</td>
<td>2.208(4)</td>
</tr>
<tr>
<td>Re1–C3</td>
<td>1.879(7)</td>
<td>Re1–P1</td>
<td>2.4648(15)</td>
</tr>
<tr>
<td>Re1–O5</td>
<td>4.235(6)</td>
<td>Re1–O6</td>
<td>3.652(5)</td>
</tr>
<tr>
<td>C1–Re1–C2</td>
<td>89.1(3)</td>
<td>C3–Re1–C1</td>
<td>89.5(3)</td>
</tr>
<tr>
<td>C3–Re1–C2</td>
<td>87.7(3)</td>
<td>N1–Re1–O4</td>
<td>78.62(17)</td>
</tr>
<tr>
<td>C1–Re1–N1</td>
<td>167.9(2)</td>
<td>C3–Re1–P1</td>
<td>93.5(2)</td>
</tr>
<tr>
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<td>100.2(2)</td>
<td>C1–Re1–P1</td>
<td>105.02(19)</td>
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<tr>
<td>C1–Re1–O4</td>
<td>92.8(2)</td>
<td>N1–Re1–P1</td>
<td>65.67(12)</td>
</tr>
<tr>
<td>S1–O4–Re1</td>
<td>133.7(3)</td>
<td>Re1–O4–S1–C21</td>
<td>145.2(5)</td>
</tr>
<tr>
<td>Re1–O4–S1–O6</td>
<td>31.3(5)</td>
<td>Re1–O4–S1–C21</td>
<td>145.2(5)</td>
</tr>
</tbody>
</table>

Fig. 3. Gas phase DFT computed spin density transitions for the vertical oxidation (a) and reduction (b) of RePNTfO.

### 3.3. Absorption and emission properties

Fig. 4a shows the absorption spectrum of RePNTfO in DCM solution. As can be seen, it has a maximum at 295 nm (ε = 7.1 × 10^3 M⁻¹ cm⁻¹) with a shoulder at 350 nm (ε = 1.8 × 10^3 M⁻¹ cm⁻¹). These absorption bands are typically assigned to intraligand (π → π⁺) and metal to ligand charge transfer (MLCT, dπ → π⁺) transitions.

For comparison, the absorption spectrum of the parent complex RePNBr was also included in Fig. 4a. It can be observed a similar shape of the bands, but an hypsochromic shift occurs when bromide is replaced by triflate.

The displacement of the MLCT band to lower energy in the case of RePNBr can be attributed to the retro-back donation effect of the bromide atom orbitals which are contributing to the HOMO orbital. Similar behavior has been reported for homologue NN-diimine coordinated complexes [51,52]. The solvent effect on the absorption band is shown in Fig. 4b.

A bathochromic shift with the polarity can be observed as typically found for MLCT bands, however the band shape lost its structure in more polar solvents. This observation motivates us to explore the possibility of replacement of the coordinated triflate by a solvent molecule, feasible when the solvent has also coordinating capabilities.

Fig. 4c demonstrates the change of the absorption spectra when a small quantity of MeCN is added to a solution of RePNTfO in air-saturated DCM solutions after excitation at 330 nm can be observed in Fig. 5a. The long Stokes Shift is consistent with a MLCT transition. The emission maximum at 535 nm of RePNTfO is blue-shifted.
when compared with the one of \textit{RePNBr} at 550 nm, which confirms the contribution of bromide orbitals to the HOMO and consistent with bands at lower energies for electron-donor ligands \cite{53}. The structureless emission band of \textit{RePNTfO} in glassy solution at 77 K shows an hypsochromic shift due to the rigidochromic effect previously reported for these kind of complexes \cite{54}, remaining at higher energy than its homologue. To confirm the replacement of the triflate group by a solvent molecule, the emission spectra in MeCN solution were recorded following its evolution in time (Fig. 5b). The initial emission band in MeCN solution, centered around 520 nm, exhibits a bathochromic shift attributed to the contribution of the \(\pi\)- acidity of the coordinated molecule of acetonitrile.

\begin{table}
\begin{tabular}{|c|c|c|}
\hline
Solvent & \(\Phi_{\text{em}}\) & \(\tau\) (ns) \\
\hline
Ethanol & 0.0005 & 2.5 \\
Dimethylformamide (DMF) & 0.0002 & 3.7 \\
MeCN & 0.0022 & 4.8 \\
\hline
\end{tabular}
\caption{Summary of photophysical properties of \textit{RePNTfO} in diverse solvents.}
\end{table}

Time resolved experiments allow us to observe a biexponential luminescent decay at 530 nm upon excitation at 300 nm in different solvents. Lifetimes, in the order of a few nanoseconds are measured in some solvents (see Table 2). The amplitude for the long \(\tau_1\) and short \(\tau_2\) components show a slight dependence with the solvent nature. These results evidence the presence of two emissive excited states, as previously described for \textit{RePNBr} \cite{13}.

For this last complex, the biexponential decay was related to the presence of two different MLCT triplet excited states very close in energy, one of those involving the pyridine orbitals \((d_{\pi} \rightarrow \pi_{py}^{*})\) and the other one, the phenyl ones \((d_{\pi} \rightarrow \pi_{ph}^{*})\) \cite{13}. It seems that
this characteristic is preserved for RePNTfO, just with shorter lifetimes probably due to the presence of the triflate ligand. As we excited at 300 nm, it is probably too, that the short component can be related to an intraligand transition. The triplet character for the emissive states was stated by measuring the singlet oxygen absorption centered at 350 nm, while the higher energy transitions times probably due to the presence of the triflate ligand. As we

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4. Conclusions

The reaction of \([P,N-(C_6H_5)_2(C_5H_4N)P]Re(CO)_3Br\) (RePNBr) with silver triflate produces the \([P,N-(C_6H_5)_2(C_5H_4N)P]Re(CO)_3(O-CF_3SO_3)\] (RePNTfO), which contains the anion directly coordinated to ReI. RePNTfO experiences one irreversible oxidation at +1.35 V (ReI/ReII) couple and three irreversible reduction processes at /C0 1.38 V, /C0 2.03 V and /C0 2.30 V (P,N-ligand). The complex in DCM solution displays a maximum at 295 nm and a shoulder around 350 nm, which corresponds to intraligand (\(\pi^*\)) and metal to ligand charge transfer (MLCT, \(d^\pi\rightarrow\pi^*\)). Excitation of RePNTfO in DCM at 350 nm leads to an emission spectrum centered at 535 nm. The change of the absorption and emission spectra in coordinating solvents compared to those observed in non-coordinating ones together with DFT/TDDFT calculations suggests that coordinating solvents replace the triflate into the coordination sphere of ReI in solution. ELF analysis confirms a very weak bond between ReI and triflate oxygen atom. Kinetics of the exchange of triflate by bromide measured in DCM at different temperatures

Table 3

<table>
<thead>
<tr>
<th>N</th>
<th>(E) (eV)</th>
<th>(\lambda) (nm)</th>
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<th>Major contributions</th>
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<tr>
<td>1</td>
<td>3.37</td>
<td>368</td>
<td>0.021</td>
<td>HOMO–1 \rightarrow LUMO (11%)</td>
</tr>
<tr>
<td>2</td>
<td>3.46</td>
<td>358</td>
<td>0.011</td>
<td>HOMO \rightarrow LUMO (88%)</td>
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<tr>
<td>3</td>
<td>3.77</td>
<td>329</td>
<td>0.021</td>
<td>HOMO \rightarrow LUMO+1 (83%)</td>
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<tr>
<td>4</td>
<td>3.80</td>
<td>318</td>
<td>0.038</td>
<td>HOMO–1 \rightarrow LUMO+1 (83%)</td>
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<tr>
<td>5</td>
<td>3.90</td>
<td>318</td>
<td>0.038</td>
<td>HOMO \rightarrow LUMO+3 (93%)</td>
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</table>

Fig. 6. DFT computed frontier orbitals HOMO–1, HOMO, LUMO and LUMO+1 plots for RePNTfO. A complete set can be found in electronic supplementary information.

Fig. 7. View of the ELF = 0.836 isosurface for RePNTfO. The region between the Re1 and O4 centers do not exhibit a disynaptic basin.

Fig. 8. ELF color-filled map with contour lines for RePNTfO in a plane defined by the O1–Re1–O4 atomic cores. Bolded lines correspond to ELF = 0.836 (inner) and ELF = 0.500 (outer). Length unit is Angstrom.

Fig. 9. Time evolution of the absorption spectrum for the reaction of RePNTfO with Br\(^{-}\). Inset: Determination of the rate constant, \(k_1\), from plot of \(k_{obs}\) vs [Br\(^{-}\)] in DCM at 20 °C.
Table 4
Rate constants and activation parameters from Eyring plot for the forward reaction of RePNTfO with bromide (Br−).

<table>
<thead>
<tr>
<th>( k_b ) ( \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1} )</th>
<th>Eyring parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 °C</td>
<td>40 °C</td>
</tr>
<tr>
<td>10.2</td>
<td>41.1</td>
</tr>
</tbody>
</table>

* Errors were lower than 10%.

allowed to estimate the Eyring parameters: \( \Delta H^* \), \( \Delta S^* \) and \( \Delta G^* \), 50.8 kJ mol\(^{-1}\), \(-109.6 \text{ J K}^{-1} \text{ mol}^{-1}\) and 83.5 kJ mol\(^{-1}\) respectively. The high negative entropy is indicative of a compact transition state, compatible with an associative mechanism, \( L_1 \) for the exchange.

Acknowledgements

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