Room-Temperature Phosphorescence and Efficient Singlet Oxygen Production by Cyclometalated Pt(II) Complexes with Aromatic Alkynyl Ligands

Ariadna Lázaro, Carla Cunha, Ramon Bosque, João Pina, Jas S. Ward, Khai-Nghi Truong, Kari Rissanen, João Carlos Lima, Margarita Crespo, J. Sérgio Seixas de Melo,* and Laura Rodríguez*

ABSTRACT: The synthesis of five novel cyclometalated platinum(II) compounds containing five different alkynyl-chromophores was achieved by the reaction of the previously synthesized Pt−Cl cyclometalated compound (1) with the corresponding RC≡CH by a Sonogashira reaction. It was observed that the spectral and photophysical characteristics of the cyclometalated platinum(II) complexes (Pt−Ar) are essentially associated with the platinum-cyclometalated unit. Room-temperature emission of the Pt−Ar complexes was attributed to phosphorescence in agreement with DFT calculations. Broad nanosecond (ns)-transient absorption spectra were observed with decays approximately identical to those obtained from the emission of the triplet state. From the femtosecond-transient absorption (fs-TA) data, two main excited-state decay components were identified: one in the order of a few picoseconds was assigned to fast intersystem crossing to populate the triplet excited-state and the second (hundreds of ns) was associated with the decay of the transient triplet state. In general, efficient singlet oxygen photosensitization quantum yields were observed from the triplet state of these complexes.

INTRODUCTION

Organometallic materials containing π-conjugated entities have emerged as a frontier research field in the past few decades, owing to their application in different fields such as organic light-emitting diodes (OLEDs), organic photovoltaic devices, and materials for nonlinear absorption. Cyclometalated complexes of late transition metals are particularly interesting in this field, mainly for their outstanding luminescent properties. Such complexes typically feature pronounced ligand-involved components (e.g., MLCT or ILCT) in their lowest triplet excited state, which facilitate radiative decays, turning emission into a competitive pathway in relation to the nonradiative relaxation processes. The photophysical properties of the cyclometalated complexes are consequently sensitively influenced by both the cyclometalated and ancillary ligands. This makes possible the convenient tailoring of the photophysical properties by modifying the ligand structures. However, heavy atom complexes that contain π-conjugated units are particularly relevant in achieving efficient nonlinear absorption by a "dual mode" pathway. This is due to the facility of harvesting triplet excited states through the spin–orbit coupling effect. In particular, it is well-known that the presence of a heavy metal ion enhances the intersystem crossing (ISC) process which is usually competitive with fluorescence. Thus, many of these types of complexes display dual fluorescence and phosphorescence.

In general, the photoexcitation of cyclometalated complexes populates initially singlet excited states (1MLCT and 1LC) and then quickly undergoes ISC to the triplet excited states with high efficiency. The lowest triplet excited state is typically described as a mixed 3MLCT/3LC state, but it can also include other states such as 3ILCT, 3LLCT, 3LMMCT, 3MMLCT, or 3MLLCT. As a result, cyclometalated complexes have gained great interest in applications in different fields such as dopants in OLEDs, photocatalysts, biological signaling compounds, optical sensors, nonlinear optical materials, solid-state light-emitting electrochemical cells, or photodynamic therapy (PDT) photosensitizers. Cyclic tetrapyrrolic structures, such as porphyrins and phthalocyanines, are one of the most intensively investigated classes of PDT photosensitizers. Nevertheless, important drawbacks have been observed in these systems, such as the long synthetic steps with low yields and the difficulty for modulating their photophysical and biological properties. These drawbacks
can be easily overcome in other complexes such as cyclo-
metalated derivatives, where the photophysical parameters can
be systematically tuned by changes of the electronic character-
istics of the complex as for porphyrins and phthalocyanines.13

One of the first reports on cyclometalated Pt(II) complexes
used for singlet oxygen sensitization was contributed by

Uncoordinated ligands are on the left and right hands of the picture. The letters in Pt−Ar (2) are used for NMR assignment.
Weinstein and co-workers in 2006\textsuperscript{14} and some other Pt(II) cyclometalated complexes with more or less efficiency have been published to date.\textsuperscript{7} The higher efficiency of Pt(II) over other heavy atoms such as Ir(III) is attributed to its square-planar geometry that avoids steric hindrances and eases the interaction with dioxygen molecule.

Taking all of this into consideration, in this work, we have designed and synthesized a series of five new Pt(II) cyclometalated compounds that differ on the ancillary ligand which is an alkynyl-chromophore. Some examples of luminescent Pt[C\textsuperscript{\textit{N}}\textsuperscript{N}C] cyclometalated complexes have already been reported in the literature, and to the best of our knowledge, in all of them the three [C\textsuperscript{\textit{N}}\textsuperscript{N}C] coordination positions belong to an aromatic cycle.\textsuperscript{15–19} The photophysical characterization of Pt[C\textsuperscript{\textit{N}}\textsuperscript{N}C] cyclometalated compounds containing a tridentate [C\textsuperscript{\textit{N}}\textsuperscript{N}C] imine ligand and alkynyl-chromophoric units occupying the fourth coordination position of the metal sphere is herein reported for the first time. Their potential as photosensitizers for singlet oxygen production was also evaluated.

\section*{RESULTS AND DISCUSSION}

\subsection*{Synthesis and Characterization.}
The syntheses of the compounds were carried out following the strategy summarized in Scheme 1 by slight modifications of the previously reported Sonogashira method.\textsuperscript{20} Parent cyclometalated compound 1 reacted with the alkynyl aromatic chromophore RC\textsubscript{\textit{=}}\textsubscript{=\!}\textsubscript{\textit{CH}} in the presence of sodium acetate as a base and Cul as a catalyst.

The compounds were obtained as orange solids after precipitation and washing with hexane in moderate to high yields (55–85\%). All compounds were characterized by mass spectra and \textsuperscript{1}H and \textsuperscript{19}F NMR spectra. \textsuperscript{1}H NMR of all compounds display the disappearance of the terminal alkynyl proton as a direct indication of coordination together with the corresponding protons of this new ancillary ligand. As previously observed, the dimethylamino protons \textsuperscript{13}H appear as a singlet around 3 ppm integrating for 6H and coupled to platinum and the imine proton is also coupled to platinum. Additionally, \textsuperscript{13}H aromatic proton is also observed to couple to platinum with a \(3J(\text{Pt–H})\) of ca. 70.2 Hz. The \textsuperscript{19}F NMR spectra show only one signal, as a broad singlet, which is not significantly affected by the exchange of chloride to alkynyl-aromatic group. A second signal is present in the NMR of compound 2b due to the aromatic \textit{p}-fluorobenzene moiety (Figures S1–S10).

Further confirmation of the successful formation of the product was gained from the C\textsubscript{\textit{\equiv}}C vibration determined by IR spectroscopy and by the determination of the protonated molecular peak in all cases recorded by ESI(+)-mass spectrometry (Figures S11–S15).

Single crystals suitable for X-ray diffraction analysis were grown for 2b, 2c, and 2d (Figure 1 and Table S1). One single molecule is present in the asymmetric units of 2b and 2d, while three independent molecules are observed in the asymmetric unit of 2c (Figure S16). Pt\textsuperscript{2+}–Pt distances are ca. 3.9 and 4.4 Å and thus, metallophilic interactions are excluded in this asymmetric unit. The unit cells, shown in Figures S17–S19A, contain 4 (2b and 2d) or 12 molecules (2c). As expected, in all cases the platinum adopts a square-planar coordination completed with the tridentate [C\textsuperscript{\textit{N}}\textsuperscript{N}C\textsuperscript{\textit{N}}] ligand and an alkynyl-chromophore ligand \textit{trans} to the imine. Bond lengths and angles are in the same range as those previously reported in the literature for Pt(II) cyclometalated complexes.\textsuperscript{11,12} The alkynyl chromophore is at a near-linear conformation with the Pt metal atom, with angles around 170–175° and its aromatic ring is almost perpendicular to the square-planar [C\textsuperscript{\textit{N}}\textsuperscript{N}C\textsuperscript{\textit{N}}]-Pt plane. The 3D packing of 2c and 2d shows intermolecular short contacts involving the fluorine atom (F(1)…H(9b) = 2.551 Å for 2c and F(1)…H(17) = 2.552 Å for 2d), while for 2b the most relevant intermolecular short contacts involve the platinum atom or the alkynyl moiety (Pt(1)…H(21) = 2.782 Å and C(15)…H(9B) = 2.689 Å), as depicted in Figures S17–S19B.

\subsection*{Electronic Spectral and Photophysical Characterization.}
The absorption spectra of the platinum(II) compounds 1 (Pt–Cl) and 2a–e (Pt–Ar) show several bands in the UV–visible range with moderate molar extinction coefficient, \(\varepsilon\), values (Figure 2 and Table 1). The lowest energy band with maxima at around 380 nm can be attributed, in agreement with previous data, to Pt(5d)–\(\pi^*\)(L) MLCT mixed
with intraligand transitions. A higher energy absorption band can be also observed in the 280−300 nm range with higher ε values. This band is also recorded for the uncoordinated alkynyl ligands, and for this reason, it can be assigned to π−π* intraligand transitions. Additional intraligand transitions typical for phenanthryl or naphthyl chromophores are buried under the absorption of the complexes. DFT theoretical calculations support these assignments (see below).

It is thus clear from the absorption spectra that the cyclometalated unit dominates the spectral features of these compounds (similar profiles were observed for 1 and 2a−e, see Figure 2), which is in agreement with the fact that (via visual observation) the new alkynyl aromatic ligands do not affect the resulting color of the powders. Moreover, the absorption spectra of the Pt−Ar complexes (Figures 2 and S20) match the excitation (Figure S21) spectra, which is a strong clue of the purity of the complexes (together with the characterization data) thus showing that the emission is due to both the Pt-cyclometalated and alkynyl-chromophoric moieties.

The luminescence spectra of the Pt−Ar compounds show a vibronically structured band centered at ca. 625 nm, found independent of the excitation wavelength (Figure 2). The recorded band presents a vibronic structure with progressional spacing of 1200 cm−1, typical of ν(C≡C) and ν(C≡N) stretching frequencies, that demonstrates the involvement of the ligand character in their emission origin. The large Stokes' shift and the quenching of the band intensity in the presence of

Table 2. Room-Temperature Photophysical Parameters for Pt−Ar and Parent Compound 1

<table>
<thead>
<tr>
<th>compound</th>
<th>ϕ_{Ph} (with O_{2})</th>
<th>ϕ_{Ph} (N_{2} sat.)</th>
<th>τ_{Ph} (ms)</th>
<th>τ_{T} (ms)</th>
<th>ϕ_{Δ} (with O_{2})</th>
<th>ϕ_{IC}</th>
<th>k_{ET} \times 10^6 (s)</th>
<th>k_{Ph} \times 10^6 (s)</th>
<th>k_{ISC}^{T_{1} \rightarrow S_{0}} \times 10^6 (s)</th>
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<tbody>
<tr>
<td>1</td>
<td>0.005</td>
<td>0.016</td>
<td>353</td>
<td>423</td>
<td>0.47</td>
<td>0.53</td>
<td>6.23</td>
<td>0.07</td>
<td>2.76</td>
</tr>
<tr>
<td>2a</td>
<td>0.005</td>
<td>0.023</td>
<td>438</td>
<td>630</td>
<td>0.21</td>
<td>0.79</td>
<td>8.21</td>
<td>0.20</td>
<td>2.09</td>
</tr>
<tr>
<td>2b</td>
<td>0.007</td>
<td>0.023</td>
<td>491</td>
<td>700</td>
<td>0.11</td>
<td>0.89</td>
<td>4.66</td>
<td>0.30</td>
<td>1.74</td>
</tr>
<tr>
<td>2c</td>
<td>0.009</td>
<td>0.018</td>
<td>357</td>
<td>650</td>
<td>0.29</td>
<td>0.71</td>
<td>1.80</td>
<td>0.06</td>
<td>1.74</td>
</tr>
<tr>
<td>2d</td>
<td>0.008</td>
<td>0.025</td>
<td>464</td>
<td>700</td>
<td>0.12</td>
<td>0.88</td>
<td>4.38</td>
<td>0.31</td>
<td>1.85</td>
</tr>
<tr>
<td>2e</td>
<td>0.008</td>
<td>0.028</td>
<td>379</td>
<td>1200</td>
<td>0.16</td>
<td>0.84</td>
<td>4.32</td>
<td>0.22</td>
<td>1.51</td>
</tr>
</tbody>
</table>

a Phosphorescence quantum yields, ϕ_{Ph}, and lifetimes, τ_{Ph} (obtained using the time-correlated single-photon counting technique), together with triplet-state lifetimes (from ns−ms laser flash photolysis) obtained in aerated (with O_{2}) or degassed (N_{2} saturated, N_{2} sat.) acetonitrile solutions.

b Singlet oxygen sensitization quantum yields (ϕ_{Δ}).

c Internal conversion quantum yields (ϕ_{IC}) and associated rate constants, k_{ET}, radiative phosphorescence decay, k_{Ph}, and intersystem crossing, k_{ISC}^{T_{1} \rightarrow S_{0}}. ϕ_{IC} = 1 − ϕ_{Ph} − ϕ_{Δ}, assuming ϕ_{T} ≠ 0 and unitary singlet oxygen sensitization efficiency S_{S} = ϕ_{S}/ϕ_{S} = 1 and therefore ϕ_{T} ≅ ϕ_{Δ}.

Figure 3. Room-temperature time-resolved transient triplet−triplet absorption spectra for the Pt−Ar derivatives (2a−e) and Pt−Cl (1) collected by laser flash photolysis at 355 nm (ns-TA) in degassed acetonitrile solutions.
oxygen (Table 1 and Figure S22) strongly indicate the origin of this luminescence to be the emission from the triplet state, i.e., phosphorescence. This is further confirmed from ns- and fs-TA data and DFT calculations and is characteristic of platinum complexes due to the heavy atom effect, which enhances the triplet state population and, consequently, the phosphorescence. Taking these facts into consideration as well as the same profile observed in all cases, the observed emission can be attributed to a IL that can be mixed with a MLCT transitions, involving the cyclometalated ligand. The value of the obtained lifetimes for the Pt–Ar complexes, in the range 430–580 ns (Table 2), supports a triplet origin where the T1 → S0 transition becomes significantly allowed by the presence of the enhanced spin–orbit coupling induced by Pt metal atom.

The phosphorescence quantum yields are lower than those for other cyclometalated Pt [C=N=N] complexes reported in the literature and may be ascribed to the more flexible imine ligand in comparison with the more rigid aromatic Pt [C=N=N] compounds.\(^{15}\)

**ns-Transient Absorption.** Time-resolved transient absorption spectra in the ns- and fs-TA were recorded in order to get further insights into the characteristics of the excited states formed. The transient triplet–triplet absorption spectra recorded by laser flash photolysis at 355 nm (ns-TA) of degassed acetonitrile solutions of the Pt–Ar derivatives, in addition to ground-state depletion (in the 380–410 nm range), present intense broad triplet–triplet absorption bands ranging between 420 and 700 nm; see Figure 3. Inspection of the spectra and the data summarized in Table 1 shows that the transient triplet–triplet wavelength maxima are basically constant for the five platinum-alkynyl cyclometalated compounds 2a–e, ranging from 490 to 540 nm, thus showing that the triplet state is much more localized and essentially corresponding to a chromophore unit which is the basic structure of the Pt–Cl (1). Moreover, triplet lifetimes, \(\tau_{Ti}\), in the 630–1200 ns range were found for the Pt–Ar complexes (Table 2).

**fs-Transient Absorption.** fs-TA provides additional information on the excited-state formation and deactivation processes occurring with the Pt–Ar complexes. The fs-TA data for Pt–Ar compounds and Pt–Cl spectra are dominated by strongly overlapped positive broad transient absorption bands in the 430–690 nm range, resulting from the convolution of the singlet excited state absorption ESA\(^{(S\rightarrow S0)}\) and the triplet excited state absorption, ESA\(^{(T\rightarrow T1)}\). Although a strong overlap is observed between these characteristic bands, the spectral resemblance of the bands observed at longer delay times in the fs-TA setup with the triplet–triplet absorption spectra obtained by ns-TA (see Figure 3), together with their long-lived nature (kinetics traces not decaying within the fs-TA probe time window of ~7.6 ns), make us assign these to the excited state absorption, following intersystem crossing.

The best-fit results and representative kinetic traces of the characteristic transient absorption data are presented in Table 3 and Figure 4. In general, the experimental kinetic traces are well-fit with the sum of three exponentials: (i) a fast decay transient with values of ~200 fs; (ii) one with values ranging from 0.5 to 3.8 ps; (iii) and a long-lived transient associated with the triplet state decay that was fixed in the analysis to the triplet state lifetime obtained from the nanosecond laser flash photolysis (Table 3).

<table>
<thead>
<tr>
<th>compound</th>
<th>(k_{S1\rightarrow T1}) (ps)</th>
<th>(k_{S1\rightarrow T1} \times 10^{11}) (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5</td>
<td>9.4</td>
</tr>
<tr>
<td>2</td>
<td>2.4</td>
<td>0.8</td>
</tr>
<tr>
<td>2b</td>
<td>3.2</td>
<td>0.3</td>
</tr>
<tr>
<td>2c</td>
<td>2.9</td>
<td>1.0</td>
</tr>
<tr>
<td>2d</td>
<td>1.1</td>
<td>1.1</td>
</tr>
<tr>
<td>2e</td>
<td>3.8</td>
<td>0.4</td>
</tr>
</tbody>
</table>

*Obtained from the results of the global fit analysis to the fs-TA data of the Pt–Ar (2a–e) derivatives and Pt–Cl (1) in acetonitrile solution at 293 K.*

The fastest transient lifetimes are in good agreement with solvent relaxation time of acetonitrile (0.26 ps) and thus are assigned to the solvation dynamics,\(^ {24}\) while the 0.5–3.8 ps transient lifetimes are attributed to the decay of the singlet excited state which undergo rapid intersystem crossing \((\tau_{S1\rightarrow T1})\) to form the observed long-lived triplet state. The observed negative amplitude values associated with the 0.5–3.8 ps transient lifetimes in the wavelength region where the ESA\(^{(T\rightarrow T1)}\) occurs, together with the concentration profiles of the time constants and the distinct rise of the long-lived, 438 ns, time constant (see Figure 4 insets) supports the triplet state being formed at the expense of the singlet excited state.

The kinetic data obtained from the fs-TA experiments are in good agreement with the luminescence lifetimes obtained with nanosecond resolution from the time-correlated single photon counting (ns-TCSPC) technique, thus showing the decay from a triplet state with the \(T1 \rightarrow S0\) transition becoming significantly allowed by the presence of the enhanced spin–orbit coupling induced by Pt metal atom.

Additionally, the intersystem crossing (ISC) rate constants, \(k_{S1\rightarrow T1}\), can be calculated (assuming a unitary singlet oxygen sensitization efficiency, \(S_A = \phi_T/\phi_A = 1\) and therefore \(\phi_T \cong \phi_A\)) using the following equation:

\[
k_{S1\rightarrow T1}^{\text{ISC}} = \frac{\phi_T}{\tau_{S1\rightarrow T1}}
\]

where the decay time and the quantum yield were obtained in aerated (presence of \(O_2\)) conditions. The obtained \(k_{S1\rightarrow T1}^{\text{ISC}}\) values support the fast triplet state formation in the Pt–Ar (2a–e) complexes (Table 3).

**Singlet Oxygen Production.** The quantum yields of singlet oxygen sensitization for the Pt–Ar (2a–e) and the precursor Pt–Cl (1) were obtained by comparison of the near-infrared phosphorescence signal of \(^3O_2\) at 1270 nm with that obtained for 1H-phenalen-1-one as reference (Table 2). Measurements were carried out in aerated acetonitrile solutions of the Pt–Ar complexes at room temperature.

It can be observed that the \(\phi_A\) values obtained for the alkynyl ligands are 4 times higher than those of the corresponding platinum complexes (see the comparison between Pt–Np (2d) and Np and Pt–Phen (2e) and Phen; Table S2). The obtained \(\phi_A\) values are more than 1 order of magnitude less than those measured for other platinum complexes recently reported in the literature\(^ {25,26}\) and in the same order of the produced by recently reported Pt(II) complexes displaying efficient biological activity.\(^ {10,28,29}\) Thus, in this case, the flexibility of the current [C=N=N] ligand does not negatively affect (decrease) the resulting \(\phi_A\) values.
It seems that the presence of the platinum heavy atom increases the efficiency of the intersystem crossing (ISC) from $^1$PS* to $^3$PS* (PS = photosensitizer) and the long-lived triplet state of PS ($^3$PS*) is a crucial component for the generation of $^{1}$O$_2$, and for this, its importance is increasing in the last years and some examples have been found with very high $^{1}$O$_2$ photogeneration, being the Pt(II) species in the majority of the cases, attached to a macrocyclic structure (porphyrin or calixarene).

From the values of the room-temperature phosphorescence quantum yields obtained in the presence, $\phi_{Ph}$, and absence, $\phi_{Ph}^0$, of oxygen, the following Stern–Volmer type relation can be retrieved, assuming that the effect of oxygen in the singlet lifetime is negligible (which is the case; see fs-TA data and Table 3 for details):

$$\frac{\phi_{Ph}^0}{\phi_{Ph}} = 1 + \tau_{Ph}^0 k_{ET}$$

where $\tau_{Ph}^0$ is the phosphorescence decay time obtained in deaerated conditions and $k_{ET}$ is the pseudo-unimolecular rate constant of energy transfer that leads to the formation of singlet oxygen ($k_{ET} = k'[O_2]$ with $[O_2]_{acetonitrile} = 1.9 \times 10^{-3}$ mol dm$^{-3}$). The values of $k_{ET}$ calculated with eq 2 are summarized in Table 2.

Additionally, the following relation can be achieved from the singlet oxygen quantum yield, $\phi_{\Delta}$, and the $\phi_{Ph}$ values obtained in the presence of oxygen:

$$\frac{\phi_{\Delta}}{\phi_{Ph}} = \frac{k_{ET}}{k_{Ph}}$$

where $k_{Ph}$ is the radiative rate constant for phosphorescence, easily obtained once $k_{ET}$ is known. Finally, in aerated conditions the rate constant for intersystem crossing $^1T_1 \rightarrow ^3S_0$, $k_{ISC}^{T_1\rightarrow S_0}$, can be calculated using the following equation

$$k_{ISC}^{T_1\rightarrow S_0} = \frac{1}{\tau_{Ph}} - k_{Ph} - k_{ET}$$

or through

$$k_{ISC}^{T_1\rightarrow S_0} = \frac{1}{\tau_{Ph}^0} - k_{Ph}$$

From Table 2 it can be seen that in the absence of oxygen the dominant excited state deactivation pathway is the radiationless internal conversion process ($\phi_{IC}$) both for Pt–Cl (1) and Pt–Ar (2a–e). Moreover, the phosphorescence quantum yields are very low even in the absence of oxygen. Interestingly, the pathway leading to singlet oxygen sensitization ($k_{ET}$) is highly competitive and always dominates with rate constants that are in some cases 4 times higher than internal conversion process, such as in the case of 2a. That is, despite the fact that the ancillary ligand does not produce noticeable effects in the range where the triplet emission occurs, it may introduce a very significant impact in the production of singlet oxygen.

The radiative rate constant for the triplet emission is also significantly affected by the aromatic ancillary ligand. Despite the values of $k_{Ph}$ always being more than 10 times lower than the internal conversion, there is a significant increase (3–4 times) in $k_{Ph}$ for compounds 2a, 2b, 2d, and 2e when compared with that of compound 1, which does not possess...
Table 4. Predicted Singlet and Triplet Transitions for All Complexes Including the Expected Wavelength and the Orbitals Involved in the Transition

<table>
<thead>
<tr>
<th>complex</th>
<th>singlet $\lambda_{em}$ (nm) ($f$)/transition</th>
<th>triplet $\lambda_{em}$ (nm)/transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>457 (0.0174) LUMO $\rightarrow$ HOMO (88%)</td>
<td>629 LUMO $\rightarrow$ HOMO (81%)</td>
</tr>
<tr>
<td>2a</td>
<td>491 (0.0008) LUMO $\rightarrow$ HOMO (98%)</td>
<td>607 LUMO $\rightarrow$ HOMO−1 (77%)</td>
</tr>
<tr>
<td>2b</td>
<td>496 (0.0012) LUMO $\rightarrow$ HOMO (98%)</td>
<td>522 LUMO $\rightarrow$ HOMO (97%)</td>
</tr>
<tr>
<td>2c</td>
<td>507 (0.0018) LUMO $\rightarrow$ HOMO (98%)</td>
<td>496 LUMO $\rightarrow$ HOMO−1 (75%)</td>
</tr>
<tr>
<td>2d</td>
<td>482 (0.2675) LUMO $\rightarrow$ HOMO (98%)</td>
<td>429 LUMO $\rightarrow$ HOMO (96%)</td>
</tr>
<tr>
<td>2e</td>
<td>514 (0.0226) LUMO $\rightarrow$ HOMO (96%)</td>
<td>608 LUMO $\rightarrow$ HOMO−1 (76%)</td>
</tr>
</tbody>
</table>

Experimental data being another evidence for phosphorescence instead of fluorescence decays. It should be noted that HOMO−1 and HOMO present some contribution of both metal and alkynyl chromophore, while the LUMO is mainly located at the ligand from the metallacycle part of the molecule. For this reason, the observed transitions can be rationalized as a mixture of $^3$IL and $^3$MLCT transitions.

## CONCLUSIONS

The synthesis and a comprehensive photophysical characterization was undertaken for five novel cyclometalated platinum(II) compounds ($\text{Pt}−\text{Ar}$, 2a−e). The absorption, emission, and excitation spectra of Pt−Ar complexes are very similar with the Pt−Cl cyclometalated compound (1) resulting in $^1$LLCT/$^1$MLCT transitions for the absorption transitions and $^1$IL and $^3$MLCT transitions for the emission. DFT calculations have been an important tool to determine the orbitals involved in these transitions. Pt−Pt interactions are not involved in the photophysical properties of the compounds in agreement with the X-ray crystal structure resolved for three of the complexes. From different time-resolved (from fs to ns) spectroscopic techniques it is found that at room temperature the deactivation of the excited state leads to a fast formation of the $T_1$ state which subsequently deactivates (phosphorescence). The excited state is found to be mainly located in the cyclometalated platinum chromophore unit. The formed triplet state of precursor 1 and the corresponding Pt−Ar derivatives has been measured and is found to efficiently sensitize molecular oxygen with values ranging from 11 to 47%.

## EXPERIMENTAL SECTION

**General.** All solvents used were spectroscopic-grade or its equivalent. Acetonitrile was purchased from Sigma-Aldrich. Deoxygenation of the solutions was done by bubbling with a stream of argon or nitrogen for approximately 20 min in a device elsewhere described. All measured solutions were freshly prepared (prior to the experiment).

All reagents were obtained from commercial sources and used as received. Ligand 4-FC$_6$H$_4$CHN(CH$_2$)$_2$N(CH$_3$)$_2$ (L) and compound [PtCl$_2$(CH$_3$)$_2$N(N(CH$_2$)$_2$N=CH(F+$\text{CH}_3$))] (1) were prepared as reported elsewhere.

**Physical Measurements.** Electrospray mass spectra were carried out at the Unitat d’Espectrometria de Masses (Universitat de Barcelona) using a LC/MSD-TOF spectrometer using H$_2$O–
CH$_3$CN 1:1 to introduce the sample. IR spectra were recorded in KBr dispersion on a FT-IR S20 Nicolet spectrophotometer. NMR spectra were carried out in CDCl$_3$, at the Unitat de RMN of the Universitat de Barcelona using a Mercury 400 spectrometer ($^1$H, 400 MHz; $^13$C, 100 MHz; $^19$F, 376.5 MHz). Chemical shifts are given in $\delta$ values (ppm) relative to TMS ($^1$H) or CFCl$_3$ ($^19$F) and coupling constants $J$ are given in Hz. Numbering schemes for the compounds characterized are displayed in Scheme 1. Absorption spectra were obtained in a 5 mm or 10 mm quartz cuvette in acetonitrile on a Cary 5000 UV-vis-NIR or Shimadzu UV-2450 spectrophotometer. The emission spectra of the compounds in solution were obtained in fluorescence quartz cuvette of 5 or 10 mm path length, using a Horiba–Jobin–Yvon Fluorolog 3.22 or Fluoromax spectrometers. Phosphorescence spectra and decays were recorded with the D1934 unit of Fluoromax 3.22 spectrometer. All the fluorescence and phosphorescence spectra were corrected for the wavelength response of the system with the appropriate correction files obtained for the instrument. Microanalyses were carried out at the Centres Científics i Tecnològics (Universitat de Barcelona).11,37

**Emission Quantum Yield Determination and Laser Flash Photolysis Experiments.** All measured solutions were degassed using a cuvette specially designed and described elsewhere for 20–30 min with N$_2$ or Ar.36 Emission quantum yields were measured with a Hamamatsu Quantaurus QY absolute photoluminescence quantum yield spectrometer model C11437 (integration sphere). 800 nm absorption spectra were measured using a flash photolysis setup composed of a LKS 60 ns laser photolysis spectrometer from Applied Photophysics, pumped with third harmonic, 355 nm, of a Spectra Physics Quanta-Ray Nd:YAG laser. The transient spectra were obtained by monitoring the optical density change at 5–10 nm intervals, averaging at least 10 decays at each wavelength.

**Singlet Oxygen Yields.** Room-temperature singlet oxygen NIR phosphorescence was detected using a Hamamatsu Q1100–42 photomultiplier in the Applied Photophysics laser flash photolysis apparatus described above. A Newport RG1000 filter was used to eliminate the harmonic contribution of sensitizer emission from the infrared signal. The singlet oxygen formation quantum yields were determined by plotting the photosensitized singlet oxygen phosphorescence intensity at 1270 nm of optically matched aerated solutions of the samples and reference compound as a function of the laser energy36 and comparing the slopes using eq 6:

$$\phi^\text{ref} = \frac{\text{slope}^\text{ref}}{\text{slope}^\text{ex}} \phi^\text{ex}$$

(6)

with $\phi^\text{ref}$ being the singlet oxygen formation quantum yield of the reference compound. 1H-Phenal-1-one in acetonitrile ($\phi^\text{ex} = 0.98$) was used as the standard.

**TCSPC.** Phosphorescence decays were obtained either in aerated or degassed aerated solutions and were measured with two different custom-built time-correlated single-photon counting equipment (TCSPC). For the Pt–Ar (2a–e) and Pt–Cl (1) compounds, ns-TCSPC was carried out as elsewhere reported except that a nanoLED (excitation at 373 nm) IBH was used as the excitation source.11 Deconvolution of the phosphorescence decay curves was performed using the modeling function method, as implemented by G. Striker in the SAND program.4

**fs-TA.** The experimental setup for ultrafast spectroscopic and kinetic measurements was described elsewhere41 and consists of a broadband HELIOS pump–probe fs-TA (350–1600 nm) spectrometer from Ultrafast Systems equipped with an amplified femtosecond Spectra-Physics Solstice-100F laser (800 nm central wavelength displaying a pulse width of 128 fs at 1 kHz repetition rate) that is coupled with a Spectra-Physics TOPAS Prime F optical parametric amplier (195–22 000 nm) for pulse pump generation. Probe light in the UV range was generated by passing a small portion of the 800 nm light from the Solstice-100F laser through a computerized optical delay (with a time window up to 8 ns) and focusing in a vertical translating CaF$_2$ crystal to generate a white-light continuum (350–750 nm). All measurements were obtained in a 2 mm quartz cuvette with absorptions lower than 0.3 at the pump excitation wavelength. The instrumental response function of the system was assumed to be equal to that of the pump–probe cross-correlation determined from the measurement of the instantaneous stimulated Raman signal from the pure solvent (in an analogous 2 mm cuvette). Typical values for the IRF of the system were found to be better than 250 fs. The solutions were stirred during the experiments or kept moving using a motorized translating sample holder in order to avoid photodegradation. The spectral chirm of the data was corrected using Surface Xplorer PRO software from Ultrafast Systems. Global analysis of the data (using a sequential model) was performed after single value decomposition using Glotaran software.42

**X-ray Diffraction.** Single crystals suitable for X-ray diffraction analysis were grown for 2b, 2c, and 2d by slow diffusion of hexane in a dichloromethane solution of the compounds. The crystal data and experimental details for the data collections are given below. Single-crystal X-ray data for 2b, 2d, and 2f were collected at 170 K on a Bruker-Nonius KappaCCD diffractometer with an APEX-II detector with graphite-monochromatised Mo-Kα ($\lambda = 0.71073$ Å) radiation. Data collection was carried out using the program COLLECT,45 with data reduction performed using HKL DENZO and SCALEPACK,44 with intensities absorption corrected using SADABS.45 All structures were solved using ShelXT,46 and refined by full-matrix least-squares on $F^2$ using SHELXL.47 in the OLEX2 program package.48 Anisotropic displacement parameters were assigned to non-H atoms. Positional disorder in the structures was treated by partly restraining geometric and anisotropic displacement parameters. All hydrogen atoms were therefore refined using riding models with $U_{	ext{dil}}(H) = 1.2U_{	ext{dil}}(C)$. CCDC 1970145–1970147 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk). Crystallographic details are given in Table S1.

**Theoretical Calculations.** DFT calculations have been performed using the Q-Chem software implemented in Spartan18,50 with the B3LYP functional and the following basis set: 6-31G*,51 including polarization for non-hydrogen atoms, for C, H, N, and Cl and LANL2DZ for Pt. Solvation effects have been included using the CPCM method.46

UV/vis transitions have been calculated at the TD-DFT level using the same functional and basis set; this methodology has provided satisfactory results in our previous work.52 To estimate the emission spectra, we have optimized the geometries corresponding to the first singlet (for fluorescence) and triplet (for phosphorescence) states and calculated the transitions between the ground state and the excited states using the corresponding excited state geometries.

**Preparation of the Complexes.** [Pt(±CpPh)(CH$_2$N(CH$_3$)$_2$N(CH$_2$)CH(CF$_3$)H$_2$)] (2a) was obtained from the reaction of 0.103 g (0.243 mmol) of [PtCl([CH$_2$N(CH$_3$)$_2$N(CH$_2$)CH(CF$_3$)H$_2$)] (1), 0.025 g (0.249 mmol) of phenylacetylene, 0.010 g (0.053 mmol) of Cul, and 0.061 g (0.744 mmol) of sodium acetate in CH$_2$Cl$_2$/methanol (10:1). The mixture was stirred at room temperature under nitrogen and protected from light for 48 h. The solvent was removed under vacuum, and the residue was treated with hexane. The orange solid was filtered and dried under vacuum. Yield: 0.091 g (76%).1 H NMR (CDCl$_3$, 400 MHz): 8.32 [s, 1H, $^3$J(Pr–H) = 81.2, H$_2$], 7.55 [d, 1H, $^5$J(F–H) = 9.6, $^8$J(H–H) = 2.3, $^3$J(Pr–H) = 70.2, H$_7$], 7.48 [d, 2H, $^5$J(H–H) = 7.1, H$_{10}$], 7.22–7.24 [m, 3H, H$_{19}$, H$_{31}$], 7.15 [t, 1H, $^7$J(H–H) = 7.4, H$_{17}$], 6.66 [dd, 1H, $^8$J(F–H) = 10.6, $^8$J(H–H) = 8.8, $^7$J(H–H) = 2.6, H$_{18}$], 4.01 [t, $^5$J(H–H) = 11.7, 2H, H$_{16}$], 3.15 [t, 2H, $^6$J(H–H) = 6.0 Hz, H$_{20}$], 3.06 [s, 6H, $^7$J(Pr–H) = 20.2, H$_{21}$].19F NMR (CDCl$_3$, 376.5 MHz): $\delta$ = −108.44 [s, 1F, MS]: m/z 490.12 [M + H$^+$], irr. $\nu$ 2097.10 (C=C=). Anal. Found: for C$_{21}$H$_{29}$N$_3$FN$_3$Pt: C 44.86 (44.93), H 3.05 (3.27), N 5.24 (5.27), S 18.50 (18.50). [Pt(±CpPh)(CH$_2$N(CH$_3$)$_2$N(CH$_2$)CH(CF$_3$)H$_2$)] (2b) was obtained as an orange solid using the same procedure from 0.102 g (0.241 mmol) of [PtCl([CH$_2$N(CH$_3$)$_2$N(CH$_2$)CH(CF$_3$)H$_2$)] (1), 0.030 g (0.249 mmol) of 1-ethynyl-4-fluorobenzene, 0.010 g (0.053 mmol)
(C0.120 mmol) of [PtCl{(CH3)2N(CH2)2NH} = 19.6, Hg]. 19F NMR (CDCl3, 376.5 MHz): δ −115.5 [s, 1F, Pt]. MS-ESI+: m/z 508.12 [M + H]+. IR: 2100.26 (C≡C). Anal. Found (calcd for C19H18F2N2Pt): C 39.07 (39.52); H 3.29 (3.48); N 5.12 (5.09).

[Pt(C≡CThio){(CH3)2N(CH2)2NH}(CH3)2N(CH2)2N] (2c) was obtained as an orange solid using the same procedure from 0.099 g (0.243 mmol) of [PtCl{(CH3)2N(CH2)2NH}(CH3)2N(CH2)2N] (1), 0.027 g (0.249 mmol) of 3-ethynyltiophene, 0.010 g (0.053 mmol) of CuI, and 0.060 g (0.731 mmol) of sodium acetate. Yield: 0.050 g (74%). 1H NMR (CDCl3, 400 MHz): δ −104.17 [s, 1F]. MS-ESI+: 590.16 [M + H]+. IR: 539.14 [M + H]+. IR: 2575.00 (C≡C).

Accession Codes
CCDC 1970145—1970147 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Author Information
Corresponding Authors
Laura Rodriguez – Departamento de Química Inorgánica y Orgánica, Sección de Química Inorgánica y Instituto de Nanociencia y Nanotecnología (IN2UB), Universitat de Barcelona, E-08028 Barcelona, Spain; orcid.org/0000-0003-0528-1967

J. Sérgio Seixas de Melo – University of Coimbra, Coimbra Chemistry Centre, Department of Chemistry, 3004-535 Coimbra, Portugal; orcid.org/0000-0001-9708-5079; Email: seeixas@ci.uc.pt

Authors
Ariadna Lázaro – Departamento de Química Inorgánica y Orgánica, Sección de Química Inorgánica y Instituto de Nanociencia y Nanotecnología (IN2UB), Universitat de Barcelona, E-08028 Barcelona, Spain

Carla Cunha – University of Coimbra, Coimbra Chemistry Centre, Department of Chemistry, 3004-535 Coimbra, Portugal

Ramon Bosque – Departamento de Química Inorgánica y Orgánica, Sección de Química Inorgánica y Instituto de Nanociencia y Nanotecnología (IN2UB), Universitat de Barcelona, E-08028 Barcelona, Spain

João Pina – University of Coimbra, Coimbra Chemistry Centre, Department of Chemistry, 3004-535 Coimbra, Portugal; orcid.org/0000-0003-1848-1167

Jas S. Ward – Jyväskylä University of Applied Sciences, Department of Chemistry, 40014 Jyväskylä, Finland; orcid.org/0000-0001-9089-9643

Khai-Nghi Truong – Jyväskylä University of Applied Sciences, Department of Chemistry, 40014 Jyväskylä, Finland

Kari Rissannen – Jyväskylä University of Applied Sciences, Department of Chemistry, 40014 Jyväskylä, Finland; orcid.org/0000-0002-7282-8419

Joaos Carlos Lima – LAQV-REQUIMTE, Departamento de Química, Universidade Nova de Lisboa, 2829-316 Monte de Caparica, Portugal; orcid.org/0000-0003-0528-1967

Margarita Crespo – Departamento de Química Inorgánica y Orgánica, Sección de Química Inorgánica y Instituto de Nanociencia y Nanotecnología, Universitat de Barcelona, E-08028 Barcelona, Spain; Institut de Biomedicina de la Universitat de Barcelona (IBUB), 08028 Barcelona, Spain; orcid.org/0000-0002-7086-9751

Notes
The authors declare no competing financial interest.

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