

# Brightly Luminescent Pt(II) Pincer Complexes with a Sterically Demanding Carboranyl-Phenylpyridine Ligand: A New Material Class for Diverse Optoelectronic Applications

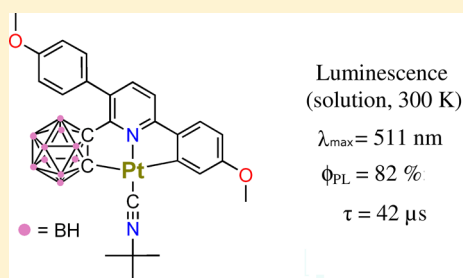
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## Supporting Information

**ABSTRACT:** A series of three Pt(II) complexes with a doubly cyclometalating terdentate ligand **L1**,  $L1H_2 = 3,6$ -bis(*p*-anisoyl)-2-carboranyl-pyridine, and diethyl sulfide (**1**), triphenylphosphine (**2**), and *t*-butylisocyanide (**3**) as ancillary ligands were synthesized. X-ray diffraction studies of **1** and **2** show a coordination of the **L1** ligand in a C–N–C mode in which the bulky and rigid *o*-carborane fragment is cyclometalated via a C atom. Importantly, no close intermolecular Pt–Pt contacts occur with this ligand type. The new Pt(II) pincer complexes display very high luminescence quantum yields at decay times of several tens of  $\mu$ s even in solution under ambient conditions. On the basis of the low-temperature ( $T = 1.3$  K) emission decay behavior, the emission is assigned to a ligand centered triplet excited state  $^3LC$  with small  $^1,^3MLCT$  admixtures. Because the phosphorescence is effectively quenched by molecular oxygen, optical sensors operating in a wide range of oxygen pressure can be developed. Owing to the very high luminescence quantum yields, the new materials might also become attractive as emitter materials for diverse optoelectronic applications.



## INTRODUCTION

Cyclometalated platinum complexes have been studied for use as electroluminescent materials in organic light emitting diodes (OLEDs),<sup>1–6</sup> as luminescent probes for bioimaging,<sup>7</sup> optical sensors,<sup>8</sup> and materials for light up-conversion.<sup>9</sup> These numerous applications in optical technologies are based on the strong luminescence displayed by such materials and the wide tunability of emission properties by chemical modifications of the molecular structures. Usually, luminescence of cyclometalated Pt(II) complexes originates from the lowest ligand-centered triplet state ( $^3LC$ ) that is moderately to strongly perturbed by admixtures with higher lying metal-to-ligand charge-transfer singlet and triplet ( $^1,^3MLCT$ ) states.<sup>1a–c,10</sup> Mixing with higher  $^1MLCT$  states induced by (indirect) spin orbit coupling (SOC)<sup>11</sup> is manifested by the amount of splitting of the lowest triplet state (zero-field splitting, ZFS) and by an increase of the radiative emission decay rate. The latter property strongly determines the utilization of a given material for particular applications.<sup>1c</sup> For instance, for use in OLEDs, usually short emission decay time is essential to minimize the saturation and, thus, efficiency roll-off effects occurring with increasing current densities.<sup>12</sup> However, also materials showing relatively long decay times at high emission quantum yields seem to be attractive for OLED applications, as has very recently been proposed.<sup>13</sup> Moreover, for sensor applications, such as oxygen sensors, making use of

diffusion controlled emission quenching, compounds exhibiting long decay times are required.<sup>14</sup>

Despite high progress achieved in the last years, engineering of highly luminescent materials showing emission quantum yields close to 100% is still a challenge. A key issue in this respect is to minimize the nonradiative depopulation of the excited states. This goal can be achieved, in particular, by designing highly rigid emitter molecules.<sup>15</sup> Thus, using cyclometalated Pt(II) complexes with ter- or tetradentate ligands seems to be a promising strategy.<sup>3–6,15</sup> However, several examples of cyclometalated Pt(II) complexes with seemingly very suitable terdentate ligands, such as dpp,  $dppH_2 = 2,6$ -diphenyl-pyridine, are nonemissive at ambient temperature.<sup>16–18</sup> Thus, for effective material engineering, a comprehensive understanding of the structural features that determine the electronic structures and excited-state molecular geometries is of high importance.

In this contribution, we describe molecular and photo-physical properties of three strongly emitting Pt(II) complexes with a new highly rigid C,N,C-cyclometalating (pincer) ligand **L1** (Figure 1) consisting of the N-coordinating pyridine and two cyclometalating fragments: *p*-anisole and *o*-carborane (= 1,2-closo-dicarbododecaborane). Carborane derivatives have been extensively studied as ligands for numerous metal

Received: March 31, 2014

Published: June 17, 2014

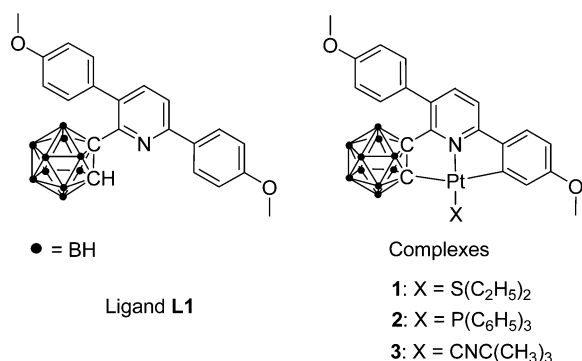


Figure 1. Molecular formulas of the studied compounds.

complexes.<sup>19,20</sup> In particular, carboranes are able to form metal–carbon<sup>21</sup> and metal–boron<sup>22</sup> bonds, respectively, which can be utilized for engineering of various cyclometalated complexes. In the new complexes with ligand L1, the particular role of *o*-carborane is to provide a highly rigid redox-inactive cyclometalating fragment. The bulky *o*-carborane cage will also prevent formation of close metal–metal contacts in solution as well as in the condensed phase, thus minimizing aggregation induced emission quenching.<sup>23</sup>

## EXPERIMENTAL SECTION

**Syntheses and Characterizations.** Detailed description of the synthetic procedures leading to the ligand L1 and the Pt-complexes 1, 2, and 3 along with the analytical data and X-ray analyses details are given in the Supporting Information.

**Photophysical Measurements.** UV–vis absorption spectra were recorded with a Varian Cary 300 double beam spectrometer. Luminescence spectra were measured with a Horiba Jobin Yvon Fluorolog 3 steady-state fluorescence spectrometer equipped with a helium cryostat (Cryovac Konti Cryostat IT), in which the helium gas flow, gas pressure, and sample holder heating were controlled. Emission decay times were recorded using a PicoQuant LDH–P-C-375 pulsed diode laser ( $\lambda_{\text{exc}} = 372$  nm, pulse width 100 ps) as excitation source. The emission signal was detected with a cooled photomultiplier connected to a FAST ComTec multichannel scalar card with a time resolution of 250 ps. Photoluminescence quantum yields were determined with a Hamamatsu C9920–02 system equipped with a Spectralon integrating sphere. Diluted solutions of the platinum complexes ( $c \approx 10^{-5}$  M<sup>-1</sup>) in 2-methyltetrahydrofuran (MeTHF) were degassed by several pump-thaw cycles ( $p = 1 \times 10^{-5}$  mbar). Polymer films containing about 0.1 wt % of the emitter were obtained by dissolving the emitter and polymers (poly(methyl-methacrylate) (PMMA) or ethyl-cellulose (EC)) in dichloromethane and spin-coating of the solutions onto quartz glass substrates. The measurements were carried out under inert N<sub>2</sub> atmosphere.

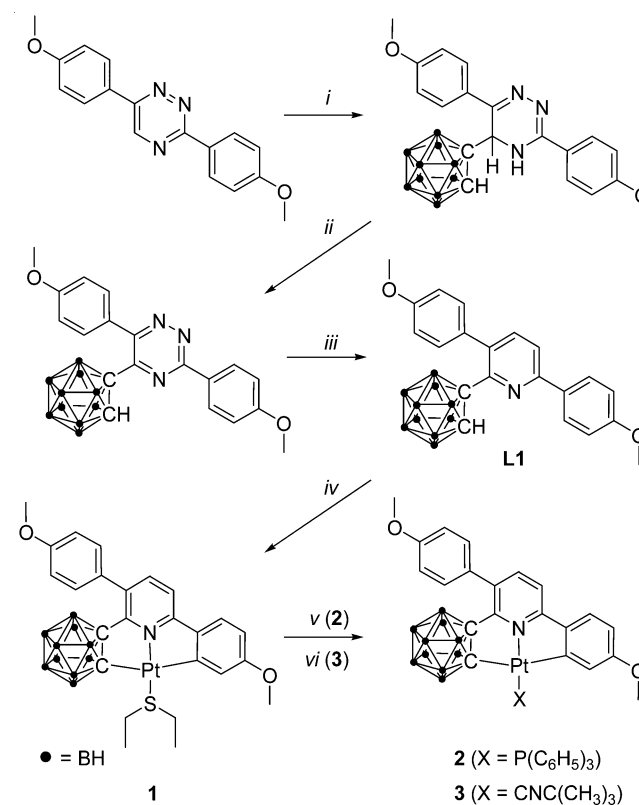
**Computational Methodology.** All calculations were carried out using the Gaussian 09 program package.<sup>24</sup> Ground state ( $S_0$ ) and the lowest triplet state ( $T_1$ ) geometries were optimized using the density functional theory (DFT) with the hybrid gradient corrected correlation functional B3LYP.<sup>25</sup> The Pople 6-31G\* atomic orbital basis set<sup>26</sup> was applied for light atoms C, H, B, O, and N, whereas the SDD<sup>27</sup> basis set augmented with three two-membered p-type polarization functions (with exponents of the contracted primitives set to 0.033 and 0.102)<sup>28</sup> was used for Pt. Inner-core electrons of Pt

were substituted by a relativistic effective core potential. The five lowest singlet and triplet electronic excitations were calculated for the ground state geometry using the time-dependent density functional theory (TD-DFT). Contour plots of molecular orbitals were generated using the GaussView program.

## RESULTS AND DISCUSSION

**Syntheses and Molecular Structures.** Ligand L1 was prepared from 3,6-di(*p*-methoxyphenyl)-1,2,4-triazine in analogy to other carboranyl-pyridines.<sup>29,30</sup> The synthetic route involves carboranylation of 3,6-di(*p*-methoxyphenyl)-1,2,4-triazine (i), rearomatization of dihydrotriazine (ii), and inverse Diels–Alder transformation of 1,2,4-triazine into pyridine (iii) (Scheme 1). Transmetalation of the in situ

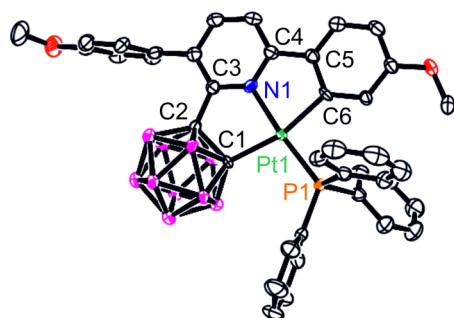
Scheme 1. Synthetic Route to the Ligand L1 and Pt(II) Complexes 1, 2, and 3<sup>a</sup>



<sup>a</sup>Reaction conditions: (i) C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>Li<sub>2</sub>, tetrahydrofuran, 40 °C, (ii) 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, CH<sub>3</sub>CO<sub>2</sub>H, 110 °C, (iii) norbornadiene, toluene, 110 °C, (iv) *n*-C<sub>4</sub>H<sub>9</sub>Li, tetrahydrofuran, 40 °C, [PtCl<sub>2</sub>(S(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>)<sub>2</sub>], 20 °C, (v) *t*-butylisocyanide, CH<sub>2</sub>Cl<sub>2</sub>, 20 °C, (vi) triphenylphosphine, CH<sub>2</sub>Cl<sub>2</sub>, 20 °C.

generated lithium salt of L1 with [PtCl<sub>2</sub>(S(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>)<sub>2</sub>] affords complex 1 (iv) in almost quantitative yield. This complex can be easily transformed to the complexes 2 and 3 by ligand exchange reactions with triphenylphosphine (v) and *t*-butylisocyanide (vi), respectively.

X-ray diffraction studies of single crystals of 1 and 3 reveal the molecular structures of the studied Pt(II) complexes, in which the metal ion is coordinated by the terdentate ligand L1 in the C,N,C-pincer mode. The fourth coordination site is occupied by the monodentate auxiliary ligand, diethyl sulfide (1; Supporting Information Figure S1) or triphenylphosphine



**Figure 2.** X-ray molecular structure of complex **2**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Pt1–C1, 2.089 Å; Pt1–N1, 2.063 Å; Pt1–C6, 2.062 Å; Pt1–P1, 2.242 Å; C1–Pt1–N1, 92.55°; N1–Pt1–C6, 81.28°; C1–Pt1–C6, 163.82°.

(**2**; Figure 2). The shortest intermolecular Pt...Pt distances found for **2** are 7.05 and 7.40 Å, respectively. This demonstrates that the ligand **L1** comprising, in particular, the bulky carboranyl fragment prevents a close approach of the metal centers in the solid phase. Thus, dimeric or chain-like structures due to metal–metal interactions cannot form.

**Electronic Absorption and Emission Properties.** UV–vis absorption spectra of the Pt complexes **1**, **2**, and **3** are composed of several strong ( $\epsilon_{\text{max}} \approx 24\,000\text{ M}^{-1}\text{ cm}^{-1}$ ) absorption bands in the near UV at  $\lambda < 350\text{ nm}$ . They are assigned to spectrally overlapping ligand-centered  $\pi\text{--}\pi^*$  transitions (corresponding to  $^1\text{LC}$  states) of the **L1** ligand and, additionally for compound **2**, to transitions occurring at the triphenylphosphine ligand. Weaker ( $\epsilon \approx 4000\text{ M}^{-1}\text{ cm}^{-1}$ ) absorption bands between about 350 and 450 nm are characterized to be of metal-to-ligand charge transfer character ( $^1\text{MLCT}$ ).<sup>1–6</sup> As an example, Figure 2 displays the absorption spectrum of complex **3** measured in 2-methyltetrahydrofuran (MeTHF) at ambient temperature.

The studied Pt(II) complexes exhibit intense green photoluminescence with very high quantum yields both in solution and in poly(methyl methacrylate) (= PMMA) films. (Table 1) The spectral positions and shapes of the emission bands showing partly resolved vibrational satellite structures are very similar to those observed for cyclometalated Pt(II) complexes with other ppy-type ligands (ppyH = 2-phenylpyridine).<sup>1b,10d,e,15</sup> This similarity implies that the luminescence properties of the Pt-L1 complexes (Figure 3) can be assigned as being dominantly related to the Pt–phenylpyridine fragment. Thus, the cyclometalated *o*-carboranyl substituent does not seem to significantly contribute to the lowest excited state. Such an assignment is also supported by the results of the TD-DFT calculations performed for compound **3**. (Supporting Information) These calculations predict that the lowest electronic transition  $S_0 \rightarrow T_1$  is mainly centered on the phenylpyridine part of the **L1** ligand with minor to moderate contributions from the metal, *t*-butylisonitrile, and the anisole methoxy substituent.

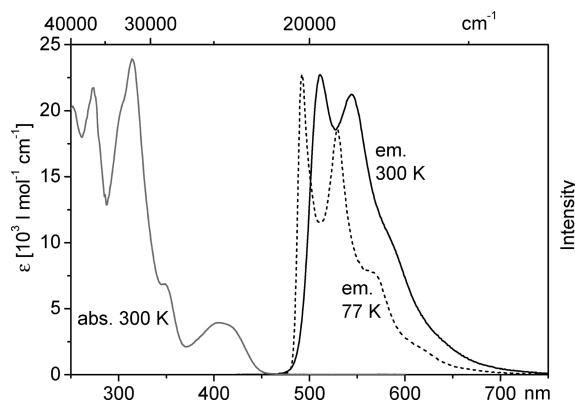
The emission decay time of the order of a few tens of  $\mu\text{s}$  indicates a phosphorescence character of the emission. The emitting state  $T_1$  is assigned to be L1-centered of  $^3\text{LC}$  character. (Compare also the general procedures for assignments of excited states as presented in ref 1c.)

For completeness it is remarked that the radiative rates  $k_r = \phi_{\text{PL}}/\tau$  of the  $T_1 \rightarrow S_0$  transitions in the complexes **1**, **2**, and **3** being in the range between  $1.4 \times 10^4\text{ s}^{-1}$  and  $2.8 \times 10^4\text{ s}^{-1}$  are

**Table 1.** Emission Wavelengths  $\lambda_{\text{max}}$ , Emission Quantum Yields  $\phi_{\text{PL}}$ , and Decay Times  $\tau$  of Complexes **1**, **2**, and **3** Measured at 300 K (and 77 K)

compound/solvent	$\lambda_{\text{max}}$ [nm] <sup>a</sup>	$\phi_{\text{PL}}$ [%]	$\tau$ [ $\mu\text{s}$ ]
1/MeTHF <sup>b</sup>	512 (492)	37 (91)	13 (32)
1/PMMA <sup>c</sup>	505	77	31
2/MeTHF <sup>b</sup>	508 (495)	1.6 <sup>d</sup> (91)	0.9 (39)
2/PMMA <sup>c</sup>	502	85	36
3/MeTHF (degassed) <sup>b</sup>	511 (492)	82 (89)	42 (43)
3/MeTHF (p(O <sub>2</sub> ) = 210 hPa) <sup>e</sup>	511	0.7	0.32
3/MeTHF (p(O <sub>2</sub> ) = 1000 hPa) <sup>f</sup>	511	0.15	0.062
3/PMMA <sup>c</sup>	506	90	42
3/EC <sup>g</sup>	509	90	42
3/powder	506	14	10 <sup>h</sup>

<sup>a</sup> $\lambda_{\text{max}}$  is the high energy emission maximum representing approximately the position of the electronic 0–0 transition. <sup>b</sup>Solutions in 2-methyltetrahydrofuran ( $c \approx 10^{-5}\text{ M}$ ) were carefully degassed by several freeze–pump–thaw cycles. <sup>c</sup>PMMA films ( $c \approx 0.1\text{ wt } \%$ ) were measured under N<sub>2</sub>-gas atmosphere. <sup>d</sup>The low quantum yield found for the  $T_1 \rightarrow S_0$  transition of compound **2** in a fluid environment is probably related to excited-state geometry changes. <sup>e</sup>Measured for air-saturated MeTHF solution, <sup>f</sup>Measured for O<sub>2</sub>-saturated MeTHF solution. <sup>g</sup>Ethoxycellulose (EC) film ( $c \approx 0.1\text{ wt } \%$ ) measured under N<sub>2</sub>-gas atmosphere. <sup>h</sup>The decay is not monoexponential. The decay time  $\tau = 10\ \mu\text{s}$  represents only an approximate value.



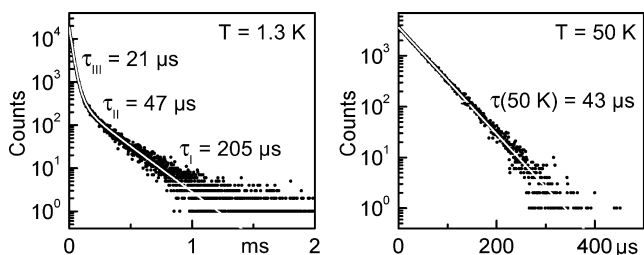
**Figure 3.** UV–vis absorption and luminescence spectra of complex **3** measured in 2-methyltetrahydrofuran (MeTHF,  $c = 5 \times 10^{-5}\text{ M}$ ) at ambient temperature and at 77 K, respectively.

significantly smaller than the respective  $k_r$  values determined for Pt(II) and Ir(III) complexes with the ppy ligand, Pt(ppy)-(dpm)<sup>10d</sup> (dpmH = dipivaloylmethane) and Ir(ppy)<sub>3</sub>,<sup>31</sup> amounting to  $1.4 \times 10^5\text{ s}^{-1}$  and  $6.9 \times 10^5\text{ s}^{-1}$ , respectively. This suggests a much smaller MLCT-perturbation of the emitting  $T_1$  state in the studied Pt-L1 complexes than in the latter compounds.<sup>1a–c</sup> Importantly, the nonradiative rate  $k_{\text{nr}} = (1 - \phi_{\text{PL}})/\tau = 2.4 \times 10^3\text{ s}^{-1}$ , as determined for **3** in poly(methyl methacrylate) (PMMA) and ethoxycellulose (EC), is very small. This is assigned to be a consequence of the rigid molecular structure of the complex and rigid local environments. Remarkably, even in solution, the nonradiative relaxation of complex **3** is very slow, as it is expressed by the small  $k_{\text{nr}}$  value of  $4.3 \times 10^3\text{ s}^{-1}$  found for **3** in 2-methyltetrahydrofuran (MeTHF) at ambient temperature. For this compound,  $k_{\text{nr}}$  decreases only by a factor of 1.6 when the temperature is lowered to 77 K and the solvent becomes stiff ( $k_{\text{nr}} = 2.6 \times 10^3\text{ s}^{-1}$ ). These observations suggest that the molecular geometry changes occurring in the  $T_1$



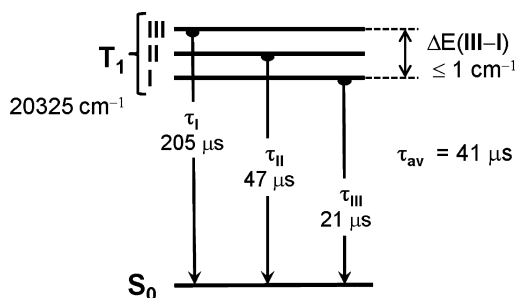
excited state of **3**, as compared to the ground state  $S_0$ , are exceptionally small. The influence of excited-state deformations on the nonradiative processes and its determining role for the emission quantum yield  $\phi_{PL}$  is further addressed below.

**Assignment of the Lowest Triplet State.** The  $^3LC$  character of the lowest triplet state is further substantiated, taking compound **3** as an example, by an analysis of the emission decay dynamics at different temperatures and quantum mechanical computations (Supporting Information). At 1.3 K, complex **3** shows a three-exponential decay profile with the time constants of  $\tau_I = 205 \mu\text{s}$ ,  $\tau_{II} = 47 \mu\text{s}$ , and  $\tau_{III} = 21 \mu\text{s}$ . (Figure 4) For a largely ligand-centered emission, the



**Figure 4.** Emission decay curves of Pt(L1)(CNC(CH<sub>3</sub>)<sub>3</sub>) (complex **3**) in frozen MeTHF at 1.3 and 50 K.

splitting (ZFS) of the  $T_1$  state into triplet substates (I, II, and III) is expected to be in the order of  $1 \text{ cm}^{-1}$  or less.<sup>1a-c,10b-d,32-34</sup> For such a small  $T_1$  splitting, the relaxations (spin–lattice relaxations<sup>32</sup>) between the triplet substates at temperatures below about 2 K are distinctly slower than the transitions to the ground state. As a result, independent emissions from the nonthermalized  $T_1$  substates are observed.<sup>10a-d,15,32,33</sup> Thus, the measured time constants  $\tau_I$ ,  $\tau_{II}$ , and  $\tau_{III}$  are identified as decay times of the individual  $T_1$  substates I, II, and III, respectively (Figure 5).

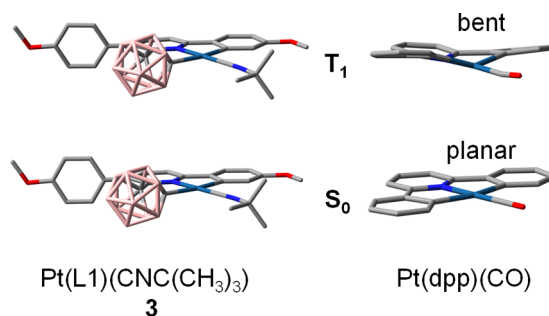


**Figure 5.** Energy level diagram for Pt(L1)(CNC(CH<sub>3</sub>)<sub>3</sub>) (**3**) in frozen MeTHF. According to the small ZFS of the  $T_1$  state and the long emission decay times at  $T = 1.3 \text{ K}$  the  $T_1$  state is assigned as being largely of  $^3LC$  character (with small  $^1,^3MLCT$  admixtures).

At higher temperatures, for example, above  $T \approx 15 \text{ K}$ , the spin–lattice relaxations are faster than the emission decay times of the individual substates.<sup>32,34</sup> Thus, the emission occurs according to an averaged decay time  $\tau_{av} = 3 \cdot (\tau_I^{-1} + \tau_{II}^{-1} + \tau_{III}^{-1})^{-1}$ .<sup>10a-d,15,31-35</sup> Insertion of the decay parameters as determined for compound **3** at 1.3 K results in  $\tau_{av} = 41 \mu\text{s}$ . This value deviates from the measured value of  $\tau(50 \text{ K}) = 43 \mu\text{s}$  only by 5% (Figure 4), that is, less than the overall experimental error of the applied methods.

**Suppression of Nonradiative Relaxation by Rigid Molecular Structures.** The occurrence of intense emissions

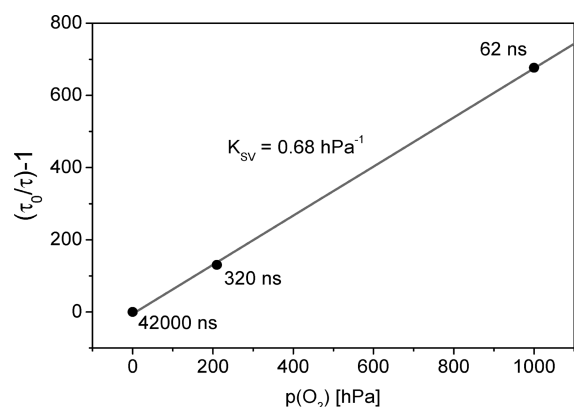
of complexes **1**, **2**, and **3** contrasts with the behavior of other Pt(II) complexes with cyclometalating C–N–C ligands, such as Pt(dpp)(CO)<sup>16</sup> and Pt(dpp)(benzoinonitrile)<sup>17,18</sup> with dppH<sub>2</sub> = 2,6-diphenyl-pyridine, which are nonemissive at room temperature. The lack of emission in these latter complexes is related to significant structural distortions occurring in the  $T_1$  excited state.<sup>18</sup> (Compare also with ref 15.) In contrast to the ground state geometry, the aromatic rings of the dpp ligand in the  $T_1$  excited state of Pt(dpp)(CO) are not coplanar and adopt a bent conformation (Figure 6, right) similar to the  $T_1$  excited molecules of Pt(dpp)(benzoinonitrile).<sup>18</sup> Such distinct molecular deformations increase the electron–vibrational coupling (Franck–Condon factors) of the excited  $T_1$  and the ground state, and thus, strongly facilitate nonradiative relaxation.<sup>1c,18,36</sup>



**Figure 6.** Molecular geometries of the ground state  $S_0$  and the lowest excited state  $T_1$  of Pt(L1)(CNC(CH<sub>3</sub>)<sub>3</sub>) (**3**) and Pt(dpp)(CO) obtained from DFT calculations on the B3LYP/(631G\*+SDD-ECP) theory level (see Supporting Information).

Apparently, such a mechanism is not effective for the relatively rigid Pt(II)-L1 complex **3** (Figure 6, left), which emits in solution with  $\phi_{PL}$  as high as 82%. On the other hand, the emission of complex **2** is largely quenched in liquid solution ( $\phi_{PL} = 1.6\%$ ). Probably, the increased nonradiative relaxation is related to the presence of a bulky ancillary ligand P(C<sub>6</sub>H<sub>6</sub>)<sub>3</sub> in **2**, as opposed to the relatively small ligands diethyl sulfide and *t*-butylisonitrile in **1** and **3**, respectively. Probably, the excited state deformations of **2** are facilitated by repulsive interactions between the sterically demanding triphenylphosphine and the terdentate ligand L1. It is remarked that in PMMA complex **2** shows very strong emission with  $\phi_{PL} = 85\%$ . Thus, in the more rigid environment of the polymer film, the emission quenching is much less effective.

**O<sub>2</sub> Sensing Properties.** The very high emission quantum yields and the long ambient-temperature emission decay times (Table 1) suggest using the studied compounds as optical O<sub>2</sub> sensors or for singlet oxygen generation. Thus, the phosphorescence quenching dynamics was investigated with complex **3** dissolved in MeTHF. As shown in Figure 7, the emission decay time varies over 3 orders of magnitude when the partial pressure of oxygen changes from  $p(\text{O}_2) = 0$  with a decay time of  $42 \mu\text{s}$  to  $p(\text{O}_2) = 1000 \text{ hPa}$  with  $\tau(\text{pure oxygen}) = 62 \text{ ns}$ . The quantum yield of emission decreases from 82% ( $p(\text{O}_2) = 0$ ) to 0.15% ( $p(\text{O}_2) = 1000 \text{ hPa}$ ). Interestingly, the emission of **3** can be still detected even at high O<sub>2</sub> concentrations. Thus, it is possible to use this material for O<sub>2</sub> detection in a wide range of  $p(\text{O}_2)$ . Application of the emitter material doped in matrices characterized by suitable gas permeability<sup>37</sup> will allow for a development of new efficient O<sub>2</sub> sensor devices.



**Figure 7.** Stern–Volmer plot for oxygen quenching of the emission of complex **3** dissolved in MeTHF ( $c = 5 \times 10^{-5}$  M) at ambient temperature. The quenching constant  $K_{SV}$  was obtained by fitting the equation:  $((\tau_0/\tau) - 1) = K_{SV} \cdot p(\text{O}_2)$ ,<sup>38</sup> wherein  $\tau_0$  and  $\tau$  are the emission decay times of the nonquenched emission ( $p(\text{O}_2) = 0$ ) and at a partial  $\text{O}_2$  pressure  $p(\text{O}_2)$ , respectively.

## CONCLUSION

A new terdentate ligand **L1** was synthesized along with three Pt(II) complexes thereof. In these complexes, the metal center is coordinated by the pyridine fragment and cyclometalated by the phenyl and carboranyl fragments in a C–N–C-pincer mode. The bulky carboranyl group prevents formation of close Pt–Pt contacts in the solid phase and in solution. The terdentate binding provides an overall rigid molecular structure of the complexes. Thus, the Pt(II) compounds display unique photophysical properties, such as very high emission quantum yields in polymer matrices and even in solution. The emission stems from a relatively long-lived ligand-centered triplet state  $T_1$  that is slightly perturbed by  $^{1,3}\text{MLCT}$  admixtures. Therefore, this new class of materials can be applied for oxygen sensors and, most interestingly, as has been discussed recently, also in a new type of electroluminescent devices<sup>13</sup> exploiting long-lived emission. For these applications, the new rigid and bulky complexes presented here might be of high significance because the material does not exhibit a tendency of aggregation even if applied at a high doping concentration in the emitter layer of an OLED.

## ASSOCIATED CONTENT

### Supporting Information

Experimental details of the syntheses, chemical analyses, X-ray crystal structure determination, ORTEP drawing of Pt-complex **1**, and results of the DFT and TD-DFT calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

The authors gratefully acknowledge Dr. M. Bodensteiner and the Center for Chemical Analysis of the Faculty of Chemistry and Pharmacy at the University of Regensburg for X-ray

diffraction measurements. We also thank the German Federal Ministry of Education and Research (BMBF) and Russian Foundation for Basic Research (RFBR) for financial support.

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