Journal Name

COMMUNICATION

Received 00th January 20xx,

Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

# Luminescence in the Solid State of Phosphine-EWO Ligands with Fluorinated Chalcone Skeletons and their $PdX_2$ complexes. Metal-promoted Phosphorescence Enhancement

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***trans*-[$PdX_2L_2$] complexes (X = Cl, Br; L = R-PEWO-$F_4$) display remarkable phosphorescent emission in the solid state, which is not observed when using $CN^-$ instead of halide, or Pt instead of Pd. DFT calculations explain these observations, illustrating the drastic effect of the metal moieties on the frontier orbitals of these structurally identical derivatives: hybridization of the moderately stable orbitals of the $PdX_2$ core with those of the chalcone fragment of the ligands is found only for the LUMO of the emissive compounds. Attending to their substantially lower lifetimes, the free ligands feature fluorescent behaviour.**

Chalcone derivatives (Ar–CH=CH–CO–Ar') are mainly known due to their biologic activity and pharmacological applications,[1] but some of them display interesting photophysical properties as well.[2] These compounds typically exhibit aggregation induced emission, determined by their lack of planarity that hinders π-stacking interactions and by *push-pull* conjugation effects at the enone moiety.[3] Very recently, a rare crystal jumping behavior was found for a highly luminescent chalcone derivative, due to a reversible intermolecular [2+2] cycloaddition process in the solid state.[4] Chemosensors with chalcone-based chromophores have been applied for the selective detection of $Cu^{2+}$ in aqueous media.[5] Applications of chalcone-derived liquid crystals for $NH_3$(g) sensing are also worth mentioning.[6]

Our pursuit of designing hemilabile ligands able to promote challenging Pd-catalysed C–C couplings (e.g. $Ar^F$–$Ar^{F'}$, $Ar^F$ = fluorinated aryl), led us to develop a family of fluorinated PEWO ligands showed in Figure 1A (PEWO = Phosphine bearing Electron-Withdrawing Olefins). The previously synthetized **$L^1$**,[9] **$L^2$**,[10] and **$L^3$** (reported here for the first time) differ in the $PR_2$ moiety (R = Ph, Cy, iPr respectively), while the analogue of **$L^1$** without fluorine substitution, labelled as **$L^4$**, was reported by Lei *et al.* (Figure 1B).[11] Clearly, these PEWO ligands feature a chalcone skeleton (highlighted in red in Figure 1).

Remarkably, the hybrid chelating ligand **$L^1$** is extremely efficient in lowering the reductive elimination barrier and also allow for oxidative addition with either ArI or ArBr (ArCl cannot be used) in catalytic conditions.[15,16] Particularly, complex [$PdCl_2L^1$] (**$2L^1$**) is an active catalyst for Negishi heterocoupling of fluorinated aryls.[17] A detailed mechanistic study of the synthesis of the [$PdCl_2L^n$] (**$2L^n$**) complexes showed that the reaction of one equivalent of L (*E*-configuration) with *trans*-[$PdCl_2$(NCMe)$_2$] quickly produces *trans*-[$PdCl_2(L^n)_2$] (**$1L^n$**, $L^n$ = **$L^1$**, **$L^2$**), observed as an intermediate in the reaction (Scheme 1).[8] The coexistence of the starting materials and complexes **$1L^n$** leads to ligand rearrangement and formation of the *E*-chelated complex (***E*-$2L^n$**), which subsequently isomerizes to the *Z* isomer, obtained selectively for **$L^1$** (**$2L^1$**). The Z-configuration of the ligand eventually triggers a C–F activation process that opens the gate to new reactivity.[21]

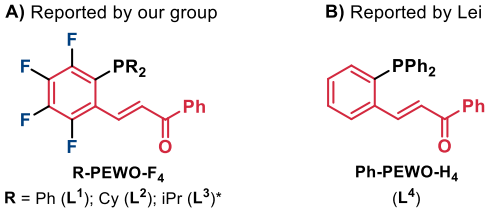


**Fig. 1**. Hybrid Phosphine-EWO ligands used in this work with the chalcone group highlighted in red. ***$L^3$** has not been previously reported.

The remarkably low activation barrier for *E/Z* olefin-isomerization (it occurs at RT) supports an extraordinary electronic delocalization of the double bond into both extremes ($C_6F_4$ and COPh) of these fluorinated chalcone structures.[8,22] The latter confirms the special *pull-pull* conjugation in our PEWO-$F_4$ ligands, that is tightly related with

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Electronic Supplementary Information (ESI) available: [synthesis and characterization of the complexes including NMR spectra, computational details and X-ray data]. CCDC 2205013-2205017. See DOI: 10.1039/x0xx00000x

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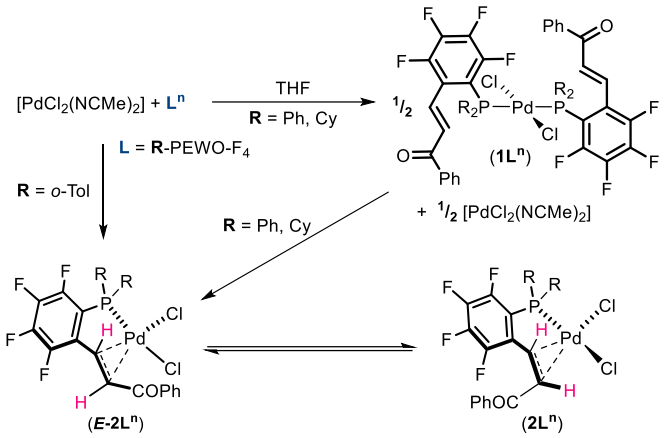
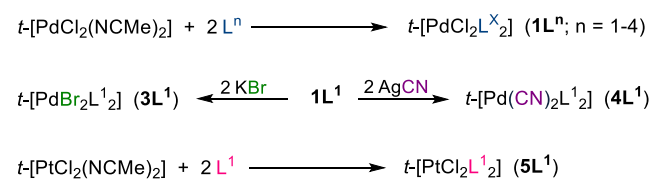
the solid-state luminescence reported in this work, displayed by the free ligands and some of their metal complexes.




**Scheme 1**. Observed intermediates in the synthesis of [$PdCl_2L^n$] (**2L$^n$**) complexes.

Complexes **1L$^{1-4}$** were selectively prepared by reaction of *trans*-[$PdCl_2(NCMe)_2$] with two equivalents of the appropriate ligand (Scheme 3, see ESI for details). X-ray structures of **1L$^1$**,[7] **2L$^1$**,[7] **L$^2$**,[8] and **1L$^4$**,[24] were already available in the literature and those of **1L$^2$** and **1L$^3$** (Figures 2 and ESI1, respectively) are reported here. The crystalline structure of ligand Ph-PEWO-$F_4$ (**L$^1$**) is also first reported in this work (Figure ESI1). Treatment of **1L$^1$** with KBr or AgCN leads to *trans*-[$PdBr_2(L^1)_2$] (**3L$^1$**) and *trans*-[$Pd(CN)_2(L^1)_2$] (**4L$^1$**), respectively. The platinum compound *trans*-[$PtCl_2(L^1)_2$] (**5L$^1$**) is synthesized analogously to **1L$^1$** (Scheme 2).




**Scheme 2**. Synthesis of complexes **1L$^n$**, **3L$^1$**, **4L$^1$** and **5L$^1$**. Note that all are *trans* compounds.

The fluorinated ligands **L$^1$** and **L$^2$** show yellow emission in the solid state upon UV irradiation, and the *E*-complexes **1L$^{1-3}$** (and **3L$^1$**) show eye-catching orange luminescence in similar conditions (Figure 2). However, the chelated *Z*-complex **2L$^1$** does not feature emissive properties. Neither the free ligands nor their complexes display emitting behaviour in solution.[25] Lack of fluorination is clearly detrimental for the luminescence (see quantum yield percentages for **L$^4$** and **1L$^4$** in Table 1) and more interestingly, both **4L$^1$** and **5L$^1$** complexes, which do not show any remarkable structural differences with **1L$^1$** are not luminescent. Figure ESI2 compare those three X-ray structures, including relevant distances within the chalcone ring (*i.e.* -C=C-) and involving the metal centres.

Table 1 collects the experimental data (excitation and emission maxima, average lifetimes, and quantum yield percentages) measured for the luminescent crystalline solids. The emission spectra as well as the decay profiles are given in the ESI (Figures ESI4-ESI13).[26] Excluding chelated *Z* complex **2L$^1$**, non-luminescent and with a drastic structural divergence, in all the other compounds (free ligands and complexes) the uncoordinated olefins have E-configuration. The chalcone moieties are submitted in the free ligands to orbital influences by the R substituents at the P atom, and, additionally, by the $MX_2$ metal fragment at which the phosphine is coordinated to in the complexes.

Concerning the free ligands, with different electronic and steric features, the highest maxima wavelength ($\lambda_{emis}$ = 606 nm) is found for the fluorinated **L$^1$** (R = Ph). For the fluorinated **L$^2$** (R = Cy, $\lambda_{emis}$ = 552 nm) the wavelength is closer to the value in **L$^4$** (R = Ph) than in **L$^1$**, as if the higher inductive effect of Cy acting as σ-donor towards the P atom was compensating, at the chalcone aryl, the electron withdrawing effect of fluorination. Apparently the two effects that increase the σ-electron density at the chalcone ring (non-fluorination and inductive effect from R) happen to diminish noticeably the quantum yield **Φ** values, to almost extinction in **L$^4$**.

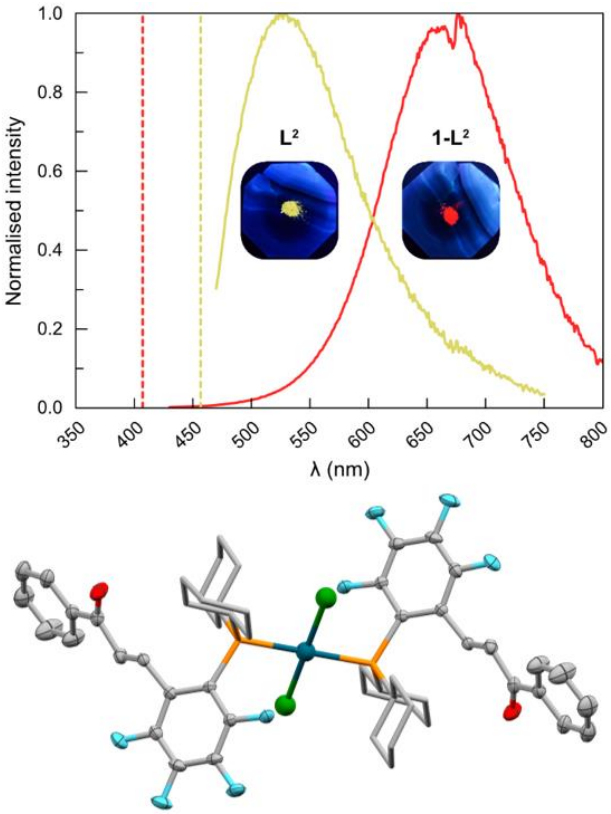



**Fig. 2**. A) Emission spectra, with normalised intensity, of **L²** (yellow line) and **1L²** (red line); dashed lines represent the maximum of excitation ($\lambda_{exc}$ in Table 1). Photographs of the ligand and complex taken upon UV irradiation are also shown. B) Molecular structure of complex **1L²** (Hs omitted for clarity) highlighting the different fragments: EWO (fluorinated chalcone) in ellipsoids, $PdCl_2$ in ball and stick while $PCy_2$ is in capped stick representation. Colour atom code: Pd (deep blue), Cl (green), P (orange), O (red), F (light blue), C (grey). Relevant distances in Å: Pd–Cl = 2.3083(8); Pd–P = 2.3295(7); C–C (olefin) = 1.324(4).

The data for the metal complexes in Table 1 show that P-coordination to the $MX_2$ fragment drastically affects the luminescence of the compounds. The coordination introduces σ-donation from the P atom to M and π-backdonation from M to P as additional modifiers of electron density on the P atom and, eventually, on the chalcone. The result on the $PdX_2$ complexes **1L$^{1-4}$** and **3L$^1$** is that they show orange-reddish



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emissions in the short 643-680 nm range for maxima. This suggests that the inductive R effect is in good part derived towards modified P donation of the coordination bond. Overall, coordination diminishes the electron density available at P for the interactions with the chalcone fragment. The observed result is higher $\lambda_{emis}$ values for complexes than for free ligands.

Table 1. Excitation and emission data of the ligands and complexes in the solid state. Instability of **L³** (when non-coordinated) precludes the corresponding luminescence analyses.

| Entry/ Comp. | $\lambda_{exc}$ (nm) | $\lambda_{emis}$ (nm)[a] | Φ (%) | $\tau_{av}$ (ns)[b] |
|---|---|---|---|---|
| 1/ **L¹** | 413 | 606 | 10.1 | 2.4 |
| 2/ **L²** | 460 | 530 | 4.1 | 3.5 |
| 3/ **L⁴** | 472 | 552 | < 3 | 3.0 |
| 4/ **1L¹** | 405 | 649 | 28.0 | $1.3 \times 10^3$ |
| 5/ **1L²** | 412 | 676 | 21.8 | $1.6 \times 10^3$ |
| 6/ **1L³** | 405 | 643 | 15.6 | $1.4 \times 10^3$ |
| 7/ **1L⁴** | 469 | 680 | < 3 | $6.4 \times 10^2$ |
| 8/ **2L¹** | *Undetected emission* | | | |
| 9/ **3L¹** | 415 | 666 | 15.7 | $5.4 \times 10^3$ |
| 10/ **4L¹** | *Undetected emission* | | | |
| 11/ **5L¹** | *Undetected emission* | | | |

[a] Very broad emission bands. [b] $\tau_{av} = (A_1\tau_1^2 + A_2\tau_2^2 + \cdots)/(A_1\tau_1 + A_2\tau_2 + \cdots)$

A positive effect of complexation to $PdCl_2$ (or $PdBr_2$ in the case of **3L¹**) is the extraordinary increase of the **Φ** range to 15-28 % values. Again, the **1L⁴** complex is hardly luminescent, supporting the importance of fluorine substituents in the chalcone ring for the emissive properties.[27] Moreover, Figure 2 shows the particular example of the Cy-PEWO-$F_4$ ligand **L²** and its corresponding $PdCl_2$ complex **1L²**. The photographs taken upon UV irradiation allow to distinguish the different emission of both compounds: yellow for the ligand and deep orange for the complex. Note that the emission bands are very broad and the $\lambda_{emis}$ is not enough to guess the colour (**L¹** is yellowish upon irradiation too, see Figure ESI3). Remarkably, this colour change is linked to a substantially higher Stokes shift for **1L²** than for **L²** (*i.e*. $9.5 \times 10^3$ $cm^{-1}$ and $2.9 \times 10^3$ $cm^{-1}$) and longer lifetimes (in the order of ms for the complexes and ns for the ligands). These observations suggest a plausible luminescence switch from fluorescence to phosphorescence upon coordination to $PdCl_2$.[28]

We were also intrigued about the orbital differences that produce the lethal effect on the luminescent behaviour of the $Pd(CN)_2$ (**4L¹**) and $PtCl_2$ (**5L1**) variants of the strongly emitting and structurally analogous $PdCl_2$ (**1L¹**) complex. Whereas **1L¹** (and the $PdBr_2$ compound **3L¹**) have two medium-strength σ-donor and slightly π-donor halide ligands, **4L¹** has more σ-donor and very strongly π-acceptor cyanide ligands. On the other hand, **5L¹** has Pt instead of Pd, and the lanthanide contraction along with the relativistic effects in Pt produce large orbital energy differences between the two isoelectronic metal centres.[29] The two cases of **4L¹** and **5L¹** are in the end roughly similar in that they are expected to have a metal centre more greedy of electron density and, consequently, less prone to be polarized.

In order to confirm our qualitative hypotheses and identify the orbitals involved in the emission, DFT calculations were carried out. Particularly, we focussed the attention in the ligand Ph-PEWO-$F_4$ (**L¹**) and the derived complexes **1L¹** (luminescent) and **4L¹**/**5L¹** (non-luminescent). As that the emissions observed do not appear in solution, geometry optimizations in the gas phase were carried out using the X-ray structures as initial guesses, leading to minimal modifications of the solid structures (full description of the computational details can be found in the ESI). First, the simulation of the absorption spectra using time-dependent DFT (TD-DFT) allows to assign the electronic transitions responsible for the excitation maxima observed in **L¹** and **1L¹**. Specifically, the computed HOMO-LUMO gap fits well the $\lambda_{exc}$ experimentally measured for **L¹** ($\lambda_{calc}$ = 402 nm; $\lambda_{exp}$ = 413 nm). While the HOMO orbital is mainly located in the $Ph_2P$ moiety (87%), the LUMO is purely a chalcone orbital (see Figure ESI15). Also, the experimental $\lambda_{exc}$ maximum of **1L¹** (*i.e*. 405 nm) fits satisfactorily the calculated transition from the HOMO-2 to the LUMO orbital ($\lambda_{calc}$ = 395 nm). In both cases the contribution of the different fragments highlighted in Figure 3 is as follows: (58% $Ph_2P$, 22% $PdCl_2$, 20% EWO) for HOMO-2, and (42% $PdCl_2$, 38% EWO, 20% $Ph_2P$) for LUMO; both are symmetrical instead of predominantly located in one of the two ligands. Remarkably, a similar transition (HOMO-2 to LUMO) in the Pt analogue **5L¹** is computed to be markedly more energetic (*i.e.* 349 nm) while the HOMO-LUMO transition for $PdCN_2$ complex **4L¹** should originate a band at a similar wavelength (*i.e* 350 nm), confirming the qualitative interpretation of similar behaviour of these two complexes.

Using TD-DFT, the emission experimentally observed for **1L¹** ($\lambda_{exp}$ = 649 nm) was assigned to the monodeexcitation from the first triplet state ($T_1$), computed to be very similar ($\lambda_{calc}$ = 667 nm). The emission band mainly involves the LUMO→HOMO phosphorescent transition (Figure 3). This is perfectly consistent with the high Stokes shift and long lifetime values commented previously (Table 1). It is worth remarking that geometry relaxation was discarded due to the very limited structural deformability allowed in the solid state.[32] Moreover, the fluorescent emissions as well as other potentially phosphorescent ones, were also computed and subsequently discarded because of numerical results far from the experimental data (details in ESI).

Evidently, deexcitation from the LUMO (42% $PdCl_2$, 38% EWO, 20% $Ph_2P$) to the $PdCl_2$ HOMO, responsible for the orange-emitting behaviour of **1L¹**, is drastically affected either in the $Pd(CN)_2$ or $PtCl_2$ analogues. Figure 3 gathers the frontier molecular orbitals (FMOs) for **1L¹**, **4L¹** and **5L¹** for comparison. Interestingly, the computed phosphorescent emissions (decay from triplet states) are experimentally unobservable, as direct consequence of the changes in the FMOs. For **5L¹**, the $PtCl_2$ HOMO resembles its $PdCl_2$ analogue but the contribution of the $PtCl_2$ fragment in the LUMO drops to the 7% (*vs* 42% for **1L¹**) and the deexcitation from the first triplet is computed to be much more energetic (*i.e*. 555 nm). The effect of the Cl by CN substitution in FMOs is also clear, with reduced participation of the $Pd(CN)_2$ fragment in the LUMO of **4L¹**



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(casually similar to the $PtCl_2$ compound) and negligible in the HOMO (Figure 3 below). After the identification of the key orbitals involved in the luminescent behaviour (mainly located in the $PdCl_2$ fragment) the data of Table 1 can be better rationalized: *i*) both the $PdBr_2$ substitution in **3L¹** (Br is well known to be electronically very similar to Cl) or the $R_2P$ modification in **1L²** and **1L³** move in the range of variations of polarization; *ii*) totally different emissions (in fact experimentally undetectable) must be expected from the $Pd(CN)_2$ (**4L¹**) or $PtCl_2$ (**5L¹**) congeners, with LUMOs hardly participated by their $MX_2$ moieties.

Finally, the computed deexcitations from the triplet states are not able to explain the experimentally observed emission of the Ph-PEWO-$F_4$ free ligand (**L¹**, $\lambda_{exp}$ = 606 nm) discarding the phosphorescent behaviour in that case. However, $S_1 \rightarrow S_0$ transition from a singlet state where a slight bending of the chalcone group is observed, afforded a satisfactory value of fluorescent emission at $\lambda_{calc}$ = 580 nm, strongly supported by the short lifetime of *ca*. 2 ns. In this case, the contribution of the $R_2P$ fragment in the orbitals involved is significant (details in ESI), and consequently the effect of the Cy substitution is appreciable (data in Table 1).

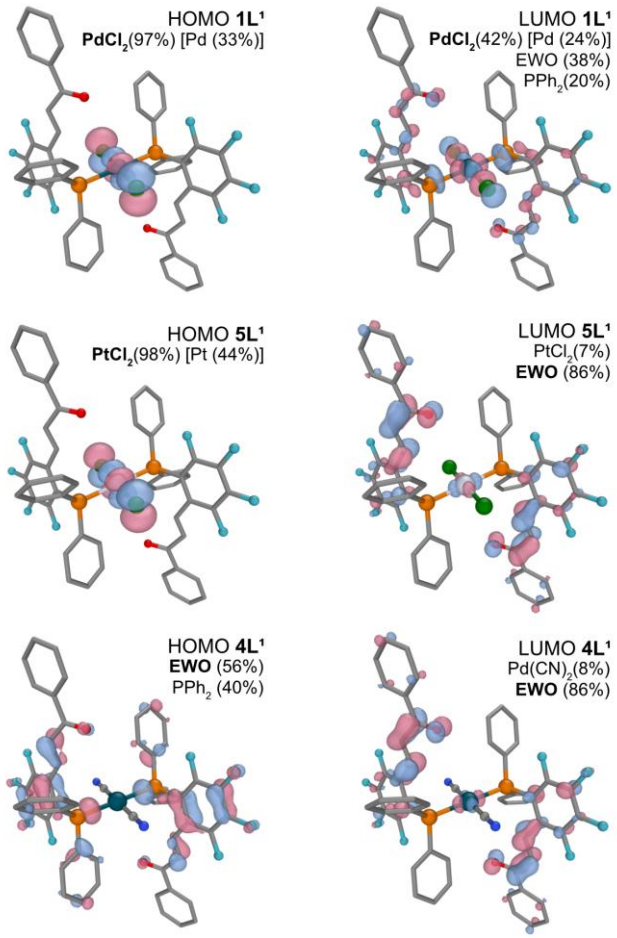


**Fig. 3**. FMOs of complexes **1L¹** (above), **5L¹** (middle) and **4L¹** (below). Contribution percentages of the different fragments are included, with the main participation in each case highlighted in bold. Relevant contributions of the metal atom (when higher than 10%) are also showed.

In summary, we have reported here a family of intensely phosphorescent palladium(II) complexes of the type *trans*-$[PdX_2L_2]$ (L = R-PEWO-$F_4$; X = Cl, Br) with quantum yields (Φ) above 15%. The orange emission is only observed in the solid state and is remarkably similar modifying the substituents in the ligand ($R_2P$ moiety with R = Ph, Cy, iPr) but the lack of fluorination in the chalcone-EWO group is clearly detrimental for the luminescent behaviour. Conversely, the non-emitting $Pd(CN)_2$ and $PtCl_2$ analogues lack the metal/chalcone connection in the LUMO orbital, directly involved in the luminescence observed for the structurally identical $PdCl_2$ (or $PdBr_2$) derivatives. DFT studies have satisfactorily reproduced the excitation and emission properties of the model compound **1L¹** and have allowed to rationalize the experimental observations upon analysis of the group contribution ($R_2P$, EWO & $MX_2$) in the key orbitals. Yellow fluorescent emission, supported by lower Stokes shifts and shorter lifetimes is also detected for the free R-PEWO-$F_4$ ligands, again intimately related with the chalcone skeleton of the EWO moiety.

We thank the Spanish MCINN (Projects PID2020-118547GB-I00 and PGC 2018-093863-B-C21) for the funding provided. J. P.-de-L. also acknowledges MCINN for a FPI studentship (BES-2017-080726). M. N. P-D. thanks Dr. Eric Mates-Torres for help and the UVa for a Margarita Salas postdoctoral fellowship (ref. CONVREC-2021-221).

## Conflicts of interest

There are no conflicts to declare.

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[29] This is reflected, for instance, in the 1st ionization energy of Pt (870 kJ/mol), considerably higher than Pd (804 kJ/mol), which exemplifies the general reluctance of Pt to diminish its electron density in shared bonds, compared to Pd.
[32] Reoptimization of both $S_1$ and $T_1$ states led to profound structural change, presumably not accessible in the crystal.

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