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Synthesis and characterization of heteroleptic cyclometalated divalent osmium $Os[P(C_6H_5)_3]_2(CO)(N\cap C^-)Cl$ complexes



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ABSTRACT

Simple synthetic procedure, reaction of $Os[P(C_6H_5)_3]_2(CO)_2Cl_2$ with 2-phenylpyridine (or other similar N∩CH chelating ligands) in boiling 2-(2-ethoxyethoxy)ethanol solution leads to $Os[P(C_6H_5)_3]_2(CO)(N∩C^-)Cl$ complexes. Structures of the obtained species have been elucidated by means of ³¹P NMR and FT-IR techniques as well as elemental analysis data. The UV-vis absorption and emission properties of the newly synthesized complexes reveal the MLCT character of their lowest singlet and triplet excited states.

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Luminescent transition-metal complexes have received in recent years a great deal of attention due to their rich photophysical properties as well as their potential applications in light-to-electricity (dyesensitized solar cells) [1–3] and electricity-to-light (OLED or PLED) [4–6] conversion devices. Among many possible metal-ligand(s) combinations, the transition-metal complexes with d⁶ or d⁸ electron configuration with various bi- or poly-dentate cyclometalated ligands (*e.g.*, 2-phenylpyridine ppy and its derivatives) forming metal-carbon bonds [7] are particularly interesting because of their well pronounced emissive properties with high quantum efficiency already at room temperature [8–14]. Strong spin-orbit coupling in these d⁶ and d⁸ complexes results in efficient intersystem crossing of the singlet state to the triplet manifold because the presence of heavy metal ion removes the spin forbidden nature of phosphorescence that results in emission from their lowest excited state.

Generally, depending on the nature of central metal ion as well as on the coordinated ligand(s) the phosphorescence may originate from the intra-ligand (IL) excited states or from the metal-to-ligand chargetransfer (MLCT) excited state [15]. The latter case seems to be especially interesting, because, upon variation of the substituents or even the skeletal designs the coordinated ligand(s), one can tune the luminescent properties of organometallic phosphors, particularly the emission wavelengths, efficiencies, and life-times [16]. This can be done changing the main coordinated chromophore involved into the MLCT transition and/ or the auxiliary ligand(s). In particular cases it may result in design of phosphors showing efficient luminescence in the near infrared (NIR) region at wavelengths longer than 700 nm as well as in saturated blue or even near-UV phosphorescent materials. In this latter respect the presence of the auxiliary ligands like CO or phosphines may distinctly improve the photophysical properties of organometallic emitters because ligands with great π -accepting character stabilize the occupied metal-based orbitals with parallel destabilization of the metal-centered excited states due to the strong back-bonding properties of π -acid ligands. The first of these effects usually leads to hypsochromic shifts of the ^{3*}MLCT emission whereas the second may block undesirable non-radiative deactivation of the ^{3*}MLCT \rightarrow dd inter-system crossing.

Both of the above mentioned effects may result in essential enhancement of the emission quantum yield as it, for example, was observed for the $Os(bpy)_3^{2+}$ complex where one of the coordinated 2.2'-bipirvdyl molecule was replaced by the bidentate phosphine ligand cis-1.2bis(diphenylphosphino)ethylene – dppv [17,18]. The resulting $Os(bpy)_2(dppv)^{2+}$ chelate, unlike $Os(bpy)_3^{2+}$, shows very intense room-temperature luminescence with an emission quantum yield three orders of magnitude greater than that of $Os(bpy)_3^{2+}$. Extremely large emission quantum efficiencies have also been found for $Os(N \cap N)(P \cap P)(CO)Cl^+$ cations where $N \cap N$ and $P \cap P$ are coordinated 1,10-phenanthroline derivatives and bidentate phosphine ligands, respectively. In a similar way the cyclometalated Os2+ complexes with auxiliary CO and/or phosphine ligands are strongly emissive organometallic phosphors [19–22]. Likewise to reported for Ir³⁺ and Pt²⁺ complexes with various cyclometalated chromophores the emission properties of less elaborated osmium(II) chelates can be modified by introducing appropriate changes in the cyclometalated ligands coordinating the Os^{2+} ion [23–26].

Usually the cyclometalated Os^{2+} complexes can been prepared using $Os_3(CO)_{12}$ as starting reactant [23–26]. Typical procedures involve heating of a mixture of the carbonyl reagent and an appropriate

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chelating ligand L giving rise to *cis*-dicarbonyl complexes Os(CO)₂ L₂. The obtained intermediates $Os(CO)_2L_2$ can be further converted, after decarbonylation with freshly sublimed $(CH_3)_3NO$, to the $Os(P)(CO)L_2$, $Os(P)_2 L_2$ or $Os(P \cap P)L_2$ products by the substitution with appropriate mono- (P) or bidentate phosphines ($P \cap P$), correspondingly. Despite that three steps are required to complete the synthesis, the final products are affordable with high yields up to 70%. On the other hand one can expect that the above described procedure can be somewhat simplified if other reactants, namely $Os(P)_2(CO)_2Cl_2$ or $Os(P \cap P)(CO)_2Cl_2$, would be applied as starting materials. To check this possibility we have performed the reaction of $Os(P(C_6H_5)_3)_2(CO)_2Cl_2$ complex with a series of the cyclometalated ligands N∩C[−]. Somewhat unexpectedly, instead of the anticipated $Os[P(C_6H_5)_3](CO)(N\cap C^-)_2$ or $Os[P(C_6H_5)_3]_2$ $(N \cap C^{-})_{2}$ products we have obtained chelates with general formulae of $Os[P(C_6H_5)_3]_2(CO)(N\cap C^-)Cl$. The obtained products have been isolated and characterized. Here we present the preliminary results of our investigations.

The not commercially available Os[P(C₆H₅)₃]₂(CO)₂Cl₂ complex can be straightforwardly synthesized by refluxing of mixture K₂OsCl₆ with two-fold excess of P(C₆H₅)₃ in deoxygenated N,N-dimethylfomamide solutions for 1.5 h [27]. The resulting solution was cooled to room temperature and then precipitated into water. The precipitated white solid was filtered, dried and purified by means of column chromatography on neutral Al₂O₃ with CH₂Cl₂ and further precipitated from the eluent solution by adding *n*-hexane. It allows to remove traces of unreacted P(C₆H₅)₃. The obtained colourless crystalline solid product (obtained with a yield up to 85%) has been identified as identical to the already described in literature *trans-cis-cis*-Os[P(C₆H₅)₃]₂(CO)₂Cl₂ by means of ³¹P NMR (singlet at -10.2 ppm) and FT-IR (two bands in CO vibration region at 1955 and 2027 cm⁻¹) spectroscopy [28–30]. The applied synthetic procedure seems to be more convenient than the previously reported one because gaseous CO is not required.

The isolated $Os(P(C_6H_5)_3)_2(CO)_2Cl_2$ intermediate successfully reacted with some NOCH cyclometalated ligands (structures depicted in Fig. 1). The reactions were carried out in the deoxygenated boiling 2-(2-ethoxyethoxy)-ethanol solutions containing $Os[P(C_6H_5)_3]_2(CO)_2Cl_2$ with equimolar amount of the investigated ligand for 8-9 h [31]. The resulting reaction mixtures were then cooled to room temperature and precipitated into water. In some cases, syntheses performed with ppy or 2,4-F₂-ppy ligands, the reaction products can be also precipitated using an excess of diethyl ether. The obtained strongly luminescent solids were filtered, dried and tentatively analyzed using ³¹P NMR spectroscopy. In the recorded ³¹P NMR spectra two dominant signals have been observed, the first one corresponding to unreacted $Os[P(C_6H_5)_3]_2(CO)_2Cl_2$ and the second (singlet located in the range 3–7 ppm) attributed to the reaction product. Noteworthy no significant signals characteristic for free $P(C_6H_5)_3$ or possible $PO(C_6H_5)_3$ by-product has been detected. This fact suggests that both of $P(C_6H_5)_3$ molecules present in the starting Os $[P(C_6H_5)_3]_2(CO)_2Cl_2$ intermediate remain in the synthesized species. The ratio of the recorded ³¹P NMR signals characteristic for the investigated reactions substrate and product allows also estimating the conversion efficiency. Efficiencies as high as ca. 70–85% have been found in the case of ppy or 2,4-F₂-ppy co-reactants, whereas in the other reported cases conversions have occurred with lower, *ca.* 20–35% yields. Noteworthy, analogously performed reactions of $Os[P(C_6H_5)_3]_2(CO)_2Cl_2$ with all three ligands from the parental 2-phenyl-benzazole family were unsuccessful, contrary to their difluoro substituted derivatives. Evidently the presence of the electron withdrawing substituents is essential for an efficient formation of the Os–C bond. Perhaps, application of more drastic synthesis conditions would result in the analogous products also in the cases of unreactive 2-phenyl-benzazoles.

Products of the performed syntheses have been separated from unreacted $Os[P(C_6H_5)_3)]_2(CO)_2Cl_2$ intermediate by means of column chromatography. In most cases the synthesized complexes have been separated and purified applying silica gel with CH_2Cl_2/n -hexane (1:1 or 2:1) mixtures as eluent. However, in the cases of the products obtained in the reaction with 3,5-F₂-pbi and 2,4-F₂-pbi ligands a combination of neutral alumina with pure CH_2Cl_2 was more effective.

The isolated substances have been further characterized by means of FT-IR spectra recorded in KBr matrices. In all investigated substances only one band in the stretching region of carbonyl group has been found with a value of v_{CO} intrinsically depending on the nature of the ligand used in each specific case (cf. data in Table 1) indicating that the synthesized species must contain at least one ligand molecule in the Os^{2+} coordination sphere. This conclusion remains in nice agreement with the different emission colours observed when crude as well as isolated reaction products are irradiated with handheld UV lamp. Taking into account the above described observations one can anticipate molecular structures of the synthesized species. Assuming monomeric nature of the synthesized complexes with octahedral coordination of the central Os^{2+} ion, the two following structures, $Os[P(C_6H_5)_3]_2(CO)(N\cap C^-)Cl$ or $Os[P(C_6H_5)_3](CO)_2(N\cap C^-)Cl$, seem to be the most probable with two equivalent $P(C_6H_5)_3$ ligands in the first or two equivalent CO molecules in the second alternative [32]. Such assignment arises from single signal and single carbonyl band in the recorded ³¹P NMR and FT-IR spectra but lack of uncoordinated triphenylphosphine (or triphenylphosphine oxide) among the isolated reaction products permits to prefer the structure with two coordinated $P(C_6H_5)_3$ ligands.

The elemental analysis results, especially the ratio of C vs. N contents point unambiguously to this option. For example in the case of the complex synthesized with use of 2,4-F₂-pbo ligand it has been found C, 59.67; H, 3.85; N, 1.45; Cl, 3.76; whereas $Os[P(C_6H_5)_3]_2(CO)(2,4-F_2-pbo)Cl$ requires C, 59.55; H, 3.60; N, 1.39; Cl, 3.52%, respectively. Similar agreement has also been found for other investigated complexes. All investigated complexes seem to contain CO, Cl⁻ and N∩C⁻ ligands located in one horizontal plane whereas two $P(C_6H_5)_3$ molecules occupy both axial position.

From two possible isomers (containing CO molecule in the *trans* position *vs*. N or C⁻ subunits of the coordinated N∩C⁻ ligand, respectively) only one of them is affordable within the used synthetic procedure. Lack of crystallographic data does not allow to directly specify which one of the possible isomers is obtainable under the applied synthetic conditions. However, the available IR data allow us to prefer isomers with localization of CO molecule in the *trans* position *vs*. hetero-aromatic fragments of the coordinated N∩C⁻ ligands. This assignment is based on the observed correlation of ν_{CO} frequency with electron withdrawing character of the



Fig. 1. Structural formulae of the ligands studied and their acronyms used in the text.

Table 1

Summary of spectroscopic and photophysical data for the investigated $Os(PPh_3)_2(CO)$ Cl(N∩C⁻) complexes. Positions of ³¹P NMR signal, CO stretching vibration frequencies ν_{CO} , UV-vis absorption maxima ($\tilde{\nu}_{abs}$), molar extinction coefficients (ε_{M}), 77 K luminescence maxima ($\tilde{\nu}_{em}$), and 77 K luminescence life-times (τ_{em}). Data in CHCl₃ solutions (³¹P NMR), KBr pellets (IR), acetonitrile solutions (UV-vis absorption), and butyronitrile glasses (77 K luminescence).

Ligand N∩C [—]	³¹ P NMR ^{a)} (ppm)	$v_{CO}^{b)}$ (cm ⁻¹)	$\widetilde{\nu}_{abs}^{c)}$ (cm ⁻¹)	$\stackrel{\epsilon_M{}^{d)}}{(M^{-1}\ cm^{-1})}$	$\widetilde{\nu}_{em}^{e)}$ (cm ⁻¹)	$\substack{\tau_{em}^{(f)}}{(\mu s)}$
2,4-F ₂ -pbi	4.32	1916	25,850	2250	21,950, 20,670	12.9
3,5-F ₂ -pbi	3.58	1916	25,200	2500	20,220, 18,860	17.3
2,4-F ₂ -ppy	4.89	1915	24,700	2140	21,600, 20,450	11.1
2,4-F ₂ -pbo	4.02	1914	24,600	2580	21,100, 19,650	9.0
рру	6.15	1904	24,200	1820	20,480, 19,350	17.0
2,4-F ₂ -pbt	4.65	1902	23,010	2550	20,150, 18,800	12.0
piq	6.04	1891	20,950	3470	17,100, 16,050	18.4 ^{g)}

^{a)} Chemical shifts are referenced to 85% phosphoric acid; corresponding 31 P NMR value for Os(PPh₃)₂(CO)₂Cl₂ = -10.15 ppm.

^{b)} Only one band has been observed in CO stretching vibration region of IR spectra; corresponding ν_{CO} values for Os(PPh₃)₂(CO)₂Cl₂ are 1955 and 2028 cm⁻¹.

^{c)} Bands assigned to ^{1*}MLCT \leftarrow S₀ transition.

^{d)} $\varepsilon_{\rm M}$ values at wavenumber of UV–vis absorption maxima (column under $\tilde{\nu}_{\rm abs}$).

^{e) 3^*}MLCT \rightarrow S₀ emission with resolved vibronic structure.

f) Mono-exponential decays.

 $^{g)}$ Room temperature data in acetonitrile solutions: $\widetilde{\nu}_{em}=$ 16,550 cm $^{-1}$, $\varphi_{em}=$ 0.14, $\tau_{em}=$ 5.1 $\mu s.$

coordinated $N \cap C^-$ ligand as it can be straightforwardly deduced from the monotonic relationships between ν_{CO} and ¹*MLCT \leftarrow S₀ absorption or ${}^{3*}MLCT \rightarrow S_0$ emission maxima (cf. data in Table 1). Increase of the electron-withdrawing properties of the coordinated bidentate $N \cap C^-$ ligand results in bathochromic shift of v_{CO} from 1916 to 1890 cm⁻¹ in the investigated $Os[P(C_6H_5)_3]_2(CO)(N\cap C^-)Cl$ series indicating weakening of the C–O bond as well as strengthening of the Os–C bond in the Os−C≡O fragment of the complexes. The larger the effect, the more pronounced is the electron withdrawing character of the coordinated N∩C ligand. Because the observed changes in v_{CO} values arise from the shift of electron density from the C–O bond to the Os–C in bond one can conclude that in the studied complexes trans position vs. CO molecule is occupied by an electron-accepting moiety. Because the investigated cyclometalating $N \cap C^-$ ligands consist of two, electron-donating $(\cap C^-)$ and electron-accepting $(N \cap)$ subunits one can also conclude that the second one is trans located to the coordinating CO molecule in the studied $Os[P(C_6H_5)_3]_2(CO)(N\cap C^-)Cl$ complexes.

Due to different electronic properties of $N\cap C^-$ chelates coordinated to the Os^{2+} core, the synthesized complexes display also well pronounced changes in their photo-physical properties reflected in the recorded UV-vis absorption and emission spectra. Representative examples of the recorded UV/Vis absorption and emission spectra are presented in Figs. 2 and 3, while the numerical photophysical data are summarized in Table 1. The intra-ligand absorption bands, located in the 200–400 nm region, are broad without well-defined maxima whereas a quite well separated additional low intensity band tail into the visible accounting for the observed colours of the synthesized species. The position of this band is nicely correlated with the electron affinity of $N\cap C^-$ ligands what enables qualifying the lowest energy bands as ¹*MLCT $\leftarrow S_0$ transitions. The corresponding ³*MLCT $\leftarrow S_0$ transitions, however, have not been observed in the recorded UV-vis absorption spectra, possibly due to very low values of their molar extinction coefficients.

In a similar way the investigated substances are emissive in different ranges of UV–vis radiation, from deep red for $Os[P(C_6H_5)_3]_2(CO)(piq)Cl$ to cyan for $Os[P(C_6H_5)_3]_2(CO)(2,4-F_2-pbi)Cl$ chelate. This observation allows to attribute the observed emission to a ^{3*}MLCT \rightarrow S₀ transition as it has been further supported by emission life-time measurements (*vide infra*). Somewhat unexpectedly, however, the synthesized complexes are emissive only in solid phase or low temperature matrices. At room temperature solutions only in the case of $Os[P(C_6H_5)_3]_2(CO)(piq)Cl$ derivative quite intense broad emission centred at $\tilde{\nu}_{em} = 16,550$ cm⁻¹ has been observed. Lowering of measurement temperature to 77 K has



Fig. 2. UV–vis absorption (*left*) and emission (*right*) spectra of $Os(P(C_6H_5)_2)_2(CO)(ppy)Cl$ complex in room temperature acetonitrile solutions and 77 K butyronitrile glasses, respectively (*solid lines*). Lower part of absorption spectrum (*dotted line*) expanded by factor 100. Emission spectrum is presented in an arbitrary intensity scale.

resulted in the appearance of emission with longer life-time τ_{em} and resolved vibronic structure. Taking into account the measured emission quantum yield $\phi_{em} = 0.14$ at room temperature and the observed change of τ_{em} from 5.1 to 18.4 µs one can conclude that at liquid nitrogen temperature $Os[P(C_6H_5)_3]_2(CO)(piq)Cl$ complex is strongly emissive with ϕ_{em} as large as *ca*. 0.50. Other investigated complexes, despite lack of emissive properties in room temperature solutions, emit strongly in 77 K butyronitrile glasses. In all investigated cases the observed structured emissions were, similarly to $Os[P(C_6H_5)_3]_2(CO)(piq)Cl$, very intense with τ_{em} in the range of 10–20 µs. @Such long emission lifetimes together with the mentioned above dependence of the $\tilde{\nu}_{em}$ on the N∩C⁻ ligand nature point undoubtedly to the ³*MLCT character of the lowest excited state in $Os[P(C_6H_5)_3]_2(CO)(N∩C^-)Cl$ molecules. Very long emission lifetimes correspond also to very low, lower than



Fig. 3. UV–vis absorption (*left*) and emission (*right*) spectra of $Os(P(C_6H_5)_2)_2(CO)(piq)CI$ complex in room temperature acetonitrile solutions and 77 K butyronitrile glasses, respectively (*solid lines*). Lower part of absorption spectrum (*dotted line*) expanded by factor 50. Emission spectrum is presented in an arbitrary intensity scale.



Fig. 4. Relationship between emission maxima $\tilde{\nu}_{em}$ of Os[P(C₆H₅)₃]₂(CO)(N∩C⁻)Cl and Ir(N∩C⁻)(acac) complexes. Values of $\tilde{\nu}_{em}$ from measurements performed at 77 K in butyronitrile matrices and room temperature solutions in acetonitrile/dioxane 1:1 mixtures for osmium(II) and iridium(III) derivatives, respectively. The data for Ir(N∩C⁻)(acac) chelates are from measurements done in our laboratory (partly published in refs [35,36]). The dotted line with slope equal unity does not represent any theoretical fit and is drawn only for illustration.

 10^5 s^{-1} , values for the radiative rate constants that do not allow direct observation of ³*MLCT←S bands in ordinary UV–vis spectra.

Depending on the chemical nature of the coordinated bidentate $N\cap C^-$ ligand, the MLCT emission from $Os[P(C_6H_5)_3]_2(CO)(N\cap C^-)Cl$ species can be tuned over a broad UV-vis radiation range, similarly as it was found for the famous $Ir(N\cap C^-)(acac)$ chelates [33–38]. The observed correlation (*cf.* Fig. 4) between emission maxima of $Ir(N\cap C^-)_2(acac)$ and $Os[P(C_6H_5)_3]_2(CO)(N\cap C^-)Cl$ luminophores supports additionally the postulated MLCT nature of the lowest, singlet and triplet excited states of the Os^{2+} chelates reported in this communication. As compared to $Ir(N\cap C^-)_2(acac)$ complexes, emission maxima of $Os[P(C_6H_5)_3]_2(CO)(N\cap C^-)Cl$ derivatives with the same $N\cap C^-$ ligand are hipsochromically shifted by *ca.* 1300 cm⁻¹ suggesting that true-blue luminophores can be also affordable within this particular class of osmium(II) complexes after appropriate modification of the $N\cap C^-$ ligand present in $Os[P(C_6H_5)_3]_2(CO)(N\cap C^-)Cl$ structure.

Taking into account the relatively long emission lifetimes measured at 77 K one can straightforwardly explain the lack of room temperature emission assuming the presence of effective non-radiative deactivation of the investigated ³*MLCT states. Although the lowest triplet states in the studied $Os[P(C_6H_5)_3]_2(CO)(N\cap C^-)Cl$ luminophores have similar nature, the observed differences in Os-CO bond energies (as it is seen from $v_{\rm CO}$ values) can explain the different (as compared to other complexes reported in this study) photo-physical behaviour of $Os[P(C_6H_5)_3]_2$ (CO)(piq)Cl complex. Populating the ³*MLCT (as well as of ¹*MLCT) excited state causes a shift of the electron density from Os²⁺ center to the $N \cap C^-$ moiety, which results in a weakening of Os-CO bonding interactions. This enables radiationless deactivation through facile metalligand bond stretching or even CO elimination [39]. The latter seems to be likely because at room temperature the investigated chelates are emissive in solid phases. In the case of $Os[P(C_6H_5)_3]_2(CO)(piq)Cl$ the lowest energy of the excited ³*MLCT state together with relatively strong Os-CO bond seems to be responsible for the observation of room temperature emission in solutions. In the other investigated complexes ^{3*}MLCT energies are higher and the Os—CO bond energies are lower as compared to $Os[P(C_6H_5)_3]_2(CO)(piq)Cl$ chelate that results in extremely operative radiationless deactivation at room temperature. Lowering of temperature to 77 K leads to intense emission because thermal activation of a "loose bolt" effect might take place only at room temperature. One can also speculate that the second possible isomers of the investigated complexes (with CO molecule located in *trans* position *vs.* C⁻ in $N\cap C^-$) will better emit because *trans* interaction with stronger electron donating C⁻ fragment of $N\cap C^-$ ligands should result in stronger Os–CO bond that could prevent non-radiative room temperature deactivation of the excited Os[P(C₆H₅)₃]₂(CO)(N\cap C⁻)Cl species. This hypothesis, however, remains only a plausible option until necessary further synthetic works will be completed.

Shortly summing up, osmium(II) chlorocarbonyl complexes with additional phosphine ligand(s) are quite interesting precursors in the syntheses of novel luminescent materials. The results presented in this communication indicate that such precursors can be successfully applied for the syntheses with cyclometalated N∩C⁻ ligands in a similar way as it was previously reported for a neutral N∩N chelates. Depending on nature of the N∩C⁻ ligand attached to Os(CO)(P)₂²⁺ or Os(CO)(P∩P)²⁺ cores, one can markedly tune photophysical properties of quite easy affordable heteroleptic Os²⁺ complexes. From this point of view such materials, promising alternative for the famous cyclometalated iridium(III) chelates, need more attention.

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