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The organoplatinum complexes cis -[PtAr₂(SMe₂)₂] (Ar = p -MeC₆H₄ and p -MeOC₆H₄) and cis,cis -[Me₂Pt(μ-SMe₂)₂PtMe₂] react very easily with 1 or 2 equiv 1,1'-bis(diphenylphosphino)acetylene (= dppac), respectively, in acetone at room temperature to give the diplatinum(II) complexes [Pt₂R₄(μ-dppac)₂], in which two R₂Pt units held together by two bridging dppac ligands.

**Binuclear organoplatinum(II) complexes with double
bis(diphenylphosphino)acetylene bridges: synthesis, X-ray structure
determination, electronic structures and DFT calculations**

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Abstract

The organoplatinum complexes $cis\text{-}[\text{PtAr}_2(\text{SMe}_2)_2]$ ($\text{Ar} = p\text{-MeC}_6\text{H}_4$ and $p\text{-MeOC}_6\text{H}_4$) and $cis,cis\text{-}[\text{Me}_2\text{Pt}(\mu\text{-SMe}_2)_2\text{PtMe}_2]$ react very easily - in acetone at room temperature - with 1 or 2 equiv 1,1'-bis(diphenylphosphino)acetylene (= dppac), to give the diplatinum(II) complexes $[\text{Pt}_2\text{R}_4(\mu\text{-dppac})_2]$, (**1**, $\text{R} = \text{Me}$; **2**, $\text{R} = p\text{-MeC}_6\text{H}_4$; **3**, $\text{R} = p\text{-MeOC}_6\text{H}_4$) in which two square-planar R_2Pt units are held together by two bridging dppac ligands. All the complexes were characterized using multinuclear (^1H , ^{31}P and ^{195}Pt) NMR spectroscopy and single crystal X-ray structure determination. Investigation of electronic structures and related DFT and TD-DFT calculations supported a mixed ^1IL (intraligand charge transfer)/ $^1\text{MLCT}$ (metal-to-ligand charge transfer) for $\text{R}=\text{Me}$ and $^1\text{L}^1\text{LCT}$ (ligand-to-ligand charge transfer) for $\text{R} = p\text{-MeC}_6\text{H}_4$ and $p\text{-MeOC}_6\text{H}_4$.

Keywords: Diphosphines; Platinum; Crystal structures; DFT calculations; Electronic structures

1. Introduction

Today, design of new binuclear complexes containing bridging ligands have received much attention due to their potential applications in self-assembly [1-6], catalysis, electrical conductivity, and photoactive devices [7, 8]. Among them, Pt(II) complexes with ligands containing group 15 and 16 elements such as nitrogen, phosphorus and sulfur have attracted great interest because of their antitumor activity [9, 10] and photophysical properties [11, 12]. Phosphorus centers are especially attractive due to softer character of phosphines as compared with nitrogen and oxygen donor ligands [13], as well as to the possibility of monitoring the system through ^{31}P NMR spectroscopy. Among the phosphines, diphosphine ligands and especially acetylenic ditertiary phosphine ligands, such as $\text{R}_2\text{PC}\equiv\text{CPR}_2$ are

potentially interesting; for instance, bis(diphenylphosphino)acetylene (abbreviated as dppac) having a linear geometry with two terminal phosphine moieties and one acetylene moiety, is able to coordinate to metal centers. Dppac has been used as a bridging ligand between metals or metal clusters such as $W_2(CO)_6$, [14] Ag(I) [15], Cu-chalcogenide [16], Ru_3 -cluster [17], $Mo(CO)_4$ [18], MX_2 ($M = Pd, Pt$; $X = Cl, Br, I, SCN$) [19-21], $Pt(C_6F_5)_2$ [22], $Pt(SC_6F_5)_2$ [23], Au [24], Pt [25] and $Ru(acac)_2$ [26].

Recently, we have described the synthesis and characterization of a series of binuclear cycloplatinated(II) complexes containing two bridging dppac ligand [27], with the related cycloplatinated(IV) complexes being as the first examples. We report here the results of X-ray crystal structure analysis and spectroscopic studies of the new complexes $[R_2Pt(\mu\text{-dppac})_2PtR_2]$ ($R = Me, p\text{-MeC}_6\text{H}_4$ or $p\text{-MeOC}_6\text{H}_4$). Electronic structures along with the corresponding TD-DFT calculations of these binuclear platinum complexes are also described.

2. Experimental section

The 1H , ^{31}P and ^{195}Pt NMR spectra were recorded in $CDCl_3$ on a Bruker Avance DRX 500 MHz spectrometer. The operating frequencies and references, respectively, are shown in parentheses as follows: 1H (500 MHz, TMS), ^{31}P (202 MHz, 85% H_3PO_4), and ^{195}Pt (107 MHz, aqueous Na_2PtCl_4). The chemical shifts and coupling constants are in ppm and Hz, respectively. UV-vis studies were carried out by using a Perkin–Elmer Lambda 25 spectrophotometer with temperature control using an EYELA NCB–3100 constant temperature bath. Bis(diphenylphosphino)acetylene was commercially available while the precursor complexes *cis*- $[PtAr_2(SMe_2)_2]$ [28] ($Ar = p\text{-MeC}_6\text{H}_4$ and $p\text{-MeOC}_6\text{H}_4$) and the dimeric precursor *cis,cis*- $[Me_2Pt(\mu\text{-SMe}_2)_2PtMe_2]$ [29] were prepared according to reported procedures.

2.1 Synthesis of complexes

[Pt₂Me₄(μ-dppac)₂], 1.

This compound had been previously synthesized in the reaction of [PtMe₂(COD)] (COD = 1,5-cyclooctadiene) with dppac [30]. In this study, diplatinum complex *cis,cis*-[Me₂Pt(μ-SMe₂)₂PtMe₂] was used as a precursor instead of [PtMe₂(COD)]. To a solution of *cis,cis*-[Me₂Pt(μ-SMe₂)₂PtMe₂] (50 mg, 0.09 mmol) in acetone (15 mL), 2 equiv of bis(diphenylphosphino)acetylene (70 mg, 0.18 mmol) was added at room temperature. The mixture was stirred for 3h. The solvent was removed and a white solid was separated and dried under vacuum. Yield: 70 mg, 65%. Mp. 275 °C (decomp.). Anal. Calcd for C₅₆H₅₂P₄Pt₂: C, 54.3; H, 4.2. Found: C, 54.0; H, 4.1. δ(¹H) 0.39 [dd, ³J_{P(trans)H} = 9.1 Hz, ³J_{P(cis)H} = 6.4 Hz, ²J_{PtH} = 71.3 Hz, 12H, 2Me–Pt]; aromatic protons: 7.06–7.36 [overlapping multiplets, 40H]. δ(³¹P) 1.8 [s, ¹J_{PtP} = 1800 Hz, 4P of dppac]; δ(¹⁹⁵Pt, ¹H coupling) -3024 [t, ¹J_{PtP} = 1798 Hz, ²J_{PtH} = 70.1 Hz, 2Pt].

The following complexes were made similarly using the related starting material *cis*-[Pt(*p*-MeC₆H₄)₂(SMe₂)₂] or *cis*-[Pt(*p*-MeOC₆H₄)₂(SMe₂)₂], respectively, and dppac (mole ratio =1:1).

[Pt₂(*p*-MeC₆H₄)₄(μ-dppac)₂], 2. Yield: 70 mg, 64%. Mp. 155 °C (decomp.). Anal. Calcd for C₈₀H₆₈P₄Pt₂: C, 62.2; H, 4.4. Found: C, 62.1; H, 4.6. δ(¹H) 2.00 [s, 12H, 4 Me ligands of *p*-tolyl], aromatic protons: 6.36 [d, ³J_{H^mH^o} = 6.9 Hz, 8H, H^m of *p*-tolyl], 6.79 [dd, ³J_{H^mH^o} = 6.9 Hz, ⁴J_{PtH^o} = 4.8 Hz, ³J_{PtH^o} = 61.5 Hz, 8H, H^o of *p*-tolyl], dppac protons: 6.32–7.48 (overlapping multiplets). δ(³¹P) -3.2 [s, ¹J_{PtP} = 1696 Hz, 2P of dppac]; δ(¹⁹⁵Pt) -2925 [t, ¹J_{PtP} = 1691 Hz, 2Pt].

[Pt₂(*p*-MeOC₆H₄)₄(μ-dppac)₂], 3. Yield: 75 mg, 72% Mp. 165 °C (decomp.). Anal. Calcd for C₈₀H₆₈O₄P₄Pt₂: C, 59.8; H, 4.2. Found: C, 60.0; H, 4.3. δ(¹H) 3.52 [s, 12H, 4 Me ligands

of *p*-MeOC₆H₄], aromatic protons: 6.15 [d, $^3J_{\text{H}^m\text{H}^o} = 7.6$ Hz, 8H, H^m of *p*-MeOC₆H₄], 6.81 [dd, $^3J_{\text{H}^m\text{H}^o} = 7.6$ Hz, $^4J_{\text{PH}^o} = 4.8$ Hz, $^3J_{\text{PH}^o} = 61.9$ Hz, 8H, H^o of *p*-MeOC₆H₄], dppac protons: 6.15–7.68 (overlapping multiplets). $\delta(^{31}\text{P})$ -3.0 [s, $^1J_{\text{PtP}} = 1711$ Hz, 2P of dppac]; $\delta(^{195}\text{Pt})$ -2919 [t, $^1J_{\text{PtP}} = 1705$ Hz, 2Pt].

2.2. X-ray Structure Determination

Diffraction data were collected by the ω -scan technique on Agilent Technologies four-circle diffractometers: **1** at 130 K on a SuperNova with Atlas CCD detector, equipped with Nova microfocus CuK α radiation source ($\lambda = 1.54178$ Å), **2** at 100 K on an Xcalibur with Eos CCD detector and graphite-monochromated MoK α radiation ($\lambda = 0.71069$ Å). The data were corrected for Lorentz-polarization as well as for absorption effects [3]. Precise unit-cell parameters were determined by the least-square fit of 22692 (**1**) and 10383 (**2**) reflections of the highest intensity, chosen from the whole experiment. The structures were solved with SIR92 [31] and refined with the full-matrix least-square procedure on F² by SHELXL-2013 [32]. All non-hydrogen atoms were refined anisotropically, hydrogen atoms were placed at idealized positions and refined as ‘riding model’ with isotropic displacement parameters set at 1.2 (1.5 for methyl groups) times U_{eq} of appropriate carrier atoms. In the crystal structure of **1**, there are two symmetry-independent molecules, in one of them one of the phenyl rings is disordered over two positions with s.o.f.’s of 57/43%.

The crystals of **3** turned out to be of very poor quality, and additionally deteriorated during data collection. Despite many attempts, the best data collected are incomplete, however, the structural analysis could be performed reasonably although with a number of restraints for both geometries of phenyl rings and shapes of displacement ellipsoids. Therefore, we decided to add the data only as the supporting information (cif file). The crystals of **2** and **3** were

highly isostructural. Relevant crystal data are listed in Table S1, together with refinement details.

2.3. Computational Details

Density functional calculations were performed with the program package Gaussian03 [17] using the B3LYP level of theory [33-35]. The LANL2DZ basis set [36-39] augmented with polarization functions on all atoms except hydrogen ones was chosen (exponents were equal to 0.587, 0.364 and 0.961 for the d functions of C, P and O, respectively, and 0.8018 for the f function of Pt). The geometries of the complexes were fully optimized by employing the density functional theory without imposing any symmetry constraints. To evaluate and ensure the optimized structures of the molecules, frequency calculations were carried out using analytical second derivatives. Solvent effects of CH₂Cl₂ were taken into account using the PCM model [40, 41]. The computations of the electronic absorption spectra using time-dependent DFT (TD-DFT) were carried out at the same level. Percentage compositions of molecular orbitals and theoretical absorption spectra were plotted using Chemissian program [34]. The NBO analyses were carried out on the stationary points using the NBO 3.1 program [42] as implemented in Gaussian 03 program package.

3. Results and discussion

3.1. Complexes synthesis and characterization

The routes to synthesize the organoplatinum(II) complexes [Pt₂R₄(μ-dppac)₂], (**1**, R = Me; **2**, R = *p*-MeC₆H₄; **3**, R = *p*-MeOC₆H₄), are described in Scheme 1. Reaction of either of known starting complexes *cis*-[PtAr₂(SMe₂)₂] [28] (Ar = *p*-MeC₆H₄ and *p*-MeOC₆H₄) or *cis,cis*-[Me₂Pt(μ-SMe₂)₂PtMe₂] [29] with 1 or 2 equiv dppac, respectively, gave the dimeric

complexes $[\text{Pt}_2\text{R}_4(\mu\text{-dppac})_2]$, **1-3**, in which two R_2Pt units are held together by two bridging dppac ligands.

Scheme 1. Preparation of the diplatinum complexes **1-3**

As a typical example, complex $[\text{Pt}_2\text{Me}_4(\mu\text{-dppac})_2]$, **1** is subjected to spectroscopic characterization (see Figure 1). The ^1H NMR spectrum of **1** exhibits the expected signal assigned to the four equivalent Me groups at δ 0.39 with $^2J_{\text{PtH}} = 71.3$ Hz. In the ^{31}P NMR spectrum of **1**, the four equivalent P atoms appeared as a singlet flanked by Pt satellites at δ 1.8, with $^1J_{\text{PtP}} = 1800$ Hz; this coupling value is significantly lower than those observed for other Pt(II) dimers containing two bridging dppac ligands (e.g. $[\text{Pt}_2\text{Cl}_4(\mu\text{-dppac})_2]$ with $^1J_{\text{PtP}} = 3660$ Hz) [19, 43], in agreement with the stronger *trans* influence of methyl ligand as compared to that of Cl ligand. The $^1J_{\text{PtP}} = 1800$ Hz, obtained for complex **1**, is close to that obtained for the complex $[\text{Pt}_2(\text{C}\equiv\text{C}'\text{Bu})_4(\mu\text{-dppac})_2]$ with $^1J_{\text{PtP}} = 2269$ Hz [22].

In ^{195}Pt [^1H coupled] NMR spectrum of the complex **1** (Figure 1C), a triplet at -3024 ppm with $^1J_{\text{PtP}} = 1798$ Hz, which is in consistent with the $^1J_{\text{PtP}}$ value obtained from ^{31}P NMR is observed, which is further couples to 6 equiv H atoms with $^2J_{\text{PtH}} = 70.1$ Hz (same as the corresponding value obtained in the ^1H NMR).

Figure 1. (A) ^1H , (B) ^{31}P and (C) ^{195}Pt [^1H coupled] NMR spectra of the complex $[\text{Pt}_2\text{Me}_4(\mu\text{-dppac})_2]$, **1**. ^1H coupling ^{195}Pt NMR spectrum of complex **1** is shown.

3.2. Crystal structures

Selected bond distances (Å) and angles (°) are listed in Table S2. Molecular structures of the complexes **1** and **2** in the solid state are shown in Figure 2.

Figure 2. Molecular structures of complexes **1** (a) and **2** (b) and the atomic numbering; the ellipsoids are drawn at the 50% probability level, hydrogen atoms are represented by spheres of arbitrary radii. (c) 10-membered $\text{Pt}_2\text{P}_4\text{C}_4$ central core of dimeric complexes.

The dimeric nature of the complexes $[\text{R}_2\text{Pt}(\mu\text{-dppac})_2\text{PtR}_2]$ ($\text{R}=\text{Me}$; **1**, $p\text{-MeC}_6\text{H}_4$; **2**, or $p\text{-MeOC}_6\text{H}_4$; **3**) was clearly confirmed by the single crystal X-ray structure determination (see Figure 2). The double dppac bridges connect two Pt centers and the P_2PtR_2 core in each molecule has a distorted square planar geometry (maximum deviation from the least-squares plane through four coordinated atoms is $0.116(2)$ Å in **2**), with an average P–Pt–P angles of 95.9° and 94.6° for complexes **1** and **2**, respectively. The average of two carbon-carbon triple bond distances are 1.203 and 1.200 Å for complexes **1** and **2**, respectively. The P–C–C angles (mean values 172.7° in **1** and 174.1° in **2**) show that these fragments are almost linear. The two dppac bridges have different orientations, forming a 10-membered $\text{Pt}_2\text{P}_4\text{C}_4$ ring (see

Figure 2C). The dihedral angles between the two coordination planes are 48.35 (11)° (**1A**), 34.37(11)° (**1B**) and 38.23(10)° (**2**). The torsion angles Pt(1)–P(1)–P(3)–Pt(2) and Pt(1)–P(2)–P(4)–Pt(2) are 21.8 (A), 3.3° (B) and 119.3 (A), 106.0° (B) for complex **1**; 5.3° and 119.7° for complex **2**. A similar arrangement has been found previously in the related complexes [Pt₂X₄(μ-dppac)₂] (X = Cl, I, C₆F₅) [21, 22, 44].

The average values of Pt–P bond distances for complexes **1**, **2** and **3** (See Supplementary material) are 2.278, 2.300 and 2.281 Å and follow the order **2**>**3**>**1** in agreement with the trends found for ¹J_{PtP} values in their ³¹P NMR spectra (1800, 1696 and 1711 Hz for **1**, **2** and **3**, respectively). These results suggest that *p*-MeC₆H₄ and *p*-MeOC₆H₄ ligands exert higher *trans* influence than the Me ligand [45-47].

3.3. Absorption spectra

Absorption spectra of complexes **1-3** in dichloromethane solution are presented in Figure 3 (see Section 3.5 for full data). They show intense absorption bands in the 250–300 nm region and, on the basis of TD-DFT calculation, the bands are reasonably assigned to the mixed ¹IL (intraligand charge transfer)/¹MLCT (metal-to-ligand charge transfer) for complex **1** and L'LCT (ligand-to-ligand charge transfer) for **2** and **3**. The energy of bands in the complexes [Pt₂R₄(μ-dppac)₂], R = Me, *p*-MeC₆H₄ or *p*-MeOC₆H₄, seems to be affected by nature of the R group (substituent at the Ar group). The energy of absorption of **3** displays a slight red-shift as compared to that of **2**, which may be attributed to the replacement of Me group by OMe, having a more electron donor character than Me. No absorption band with wavelengths longer than ~400 nm was observed in absorption spectra of all complexes.

Figure 3. Absorption spectra of complexes **1-3** (2×10^{-5} M) in CH_2Cl_2 solvent.

3.4. Geometry optimizations, charge distributions, electronic structures and NBO analyses

Theoretical studies of the newly synthesized complexes and their electronic structures and bonding properties, were carried out by the DFT method. DFT geometries of the complexes **1-3** were optimized in singlet states at the B3LYP functional level of theory (Figure S1) and their optimized geometric parameters are listed in Table S2. The calculated bond distances and angles (Table S2) are in good agreement to the values obtained from X-ray crystal structure determination. Differences observed between the experimental and calculated bond lengths and angles result from the fact that computations were performed in the gas phase, whereas the X-ray data are found in solid phase. The B3LYP method appears as a reasonable compromise between demands for accuracy on the one hand, and CPU time of calculations on the other, and therefore we used it for our investigation.

Calculated positive charge on Pt atom of the methylplatinum complex **1** is significantly smaller than those on Pt centers of the arlyplatinum complexes **2** and **3** (see Table S3). However, all Pt charge values are considerably lower than the formal charge of +2, corresponding to the d^8 configuration of the central ion. There are large negative charges on the C atoms connected to Pt in complex **1**, and the charges on the P atoms of complexes **1-3** are close to zero.

Populations of d orbitals of platinum centers in the complexes **1-3** are shown in Table 1. Typically populations of $d_{xy}d_{xz}d_{yz}d_{x^2-y^2}$ and d_{z^2} of Pt(1) center orbitals in complex **1** are 1.613, 1.857, 1.873, 1.891 and 1.874, respectively, suggesting that donation from ligands to d orbitals of Pt plays a key role in electronic structure of the examined complexes.

Table 1. Populations of d orbitals of Pt atoms in complexes **1-3**

	d_{xy}	d_{xz}	d_{yz}	$d_{x^2-y^2}$	d_{z^2}
Complex 1					
Pt(1)	1.613	1.857	1.873	1.891	1.874
Pt(2)	1.498	1.824	1.934	1.918	1.935
Complex 2					
Pt(1)	1.563	1.822	1.923	1.879	1.918
Pt(2)	1.563	1.821	1.923	1.879	1.918
Complex 3					
Pt(1)	1.566	1.813	1.924	1.884	1.918
Pt(2)	1.553	1.833	1.930	1.865	1.926

Partial molecular orbital diagrams for the binuclear complexes **1-3**, with several highest occupied and lowest unoccupied molecular orbital contours are depicted in Figures 4, S2 and S3 and distribution of important frontier orbitals in the ground state and the corresponding partial molecular orbital composition (percentages) are provided in Tables 2 and S4. Values

of the HOMO–LUMO energy gaps are equal to 4.49, 4.13 and 3.83 eV for the complexes **1**, **2** and **3**, respectively. Although the lowest occupied molecular orbital of the complex [Pt₂Me₄(μ–dppac)₂], **1**, is considerably localized on the Pt centers, the HOMO of complexes [Pt₂(*p*-MeC₆H₄)₄(μ–dppac)₂], **2**, and [Pt₂(*p*-MeOC₆H₄)₄(μ–dppac)₂], **3**, are mainly localized on the *p*-MeC₆H₄ and *p*-MeOC₆H₄ groups. LUMO of complexes **1-3** are mainly localized on bridging dppac ligands.

Figure 4. Qualitative frontier molecular orbitals for complex 1.

Table 2. Energies and composition(%) of frontier MOs in ground state for the complex **1**^a

	eV	Pt(1)	Pt(2)	2Me(1)	2Me(2)	dppac(1)	dppac(2)
LUMO + 4	-0.87	3	2	1	0	30	64
LUMO + 3	-1.04	3	3	0	1	7	86
LUMO + 2	-1.09	3	1	1	0	65	29
LUMO + 1	-1.17	2	2	1	1	78	17
LUMO	-1.31	3	2	1	1	30	63
HOMO	-5.80	32	44	7	9	4	4
HOMO - 1	-5.83	41	29	11	9	4	6
HOMO - 2	-6.26	11	10	7	15	10	47
HOMO - 3	-6.30	3	23	8	12	46	9
HOMO - 4	-6.43	4	69	5	4	13	5
HOMO - 5	-6.44	85	1	0	0	9	5
HOMO - 6	-6.46	12	34	11	5	25	14

^aData for complexes **2** and **3** are collected in Table S4, see Supplementary data.

3.5. TD-DFT calculations and electronic spectra of the complexes

Table S5 (see Supplementary data) shows the most important electronic transitions assigned to the observed absorption bands of **1**, **2** and **3**, respectively, calculated with the TD-DFT method. The sequence of computed $S_0 \rightarrow S_1$ transition energies (i.e. **1**>**2**>**3**) agrees well with the observed lowest energy absorptions. The experimental and calculated electronic spectra of complex **1** are presented in Figure 5. The longest wavelength experimental band of **1** at 333 nm originates from the HOMO→LUMO (65%) and HOMO-1→LUMO (18%) transitions.; the HOMO and HOMO-1 are located at two Pt centers and LUMO is delocalized over the two bridging dppac ligands (Figure 4). Accordingly, the transition at 333 nm can be seen as a delocalized MLCT (Metal-to-Ligand CT) transition.

Figure 5. Experimental and calculated (bars) electronic absorption spectra of complex **1**.

Computed high energy absorption bands for complex **2** at 275 nm (HOMO-12 $\rightarrow$ LUMO (41%) + (HOMO $\rightarrow$ LUMO+11 (24%)) and for complex **3** at 287 nm (HOMO-1 $\rightarrow$ LUMO+12 (32%) + HOMO $\rightarrow$ LUMO + 14 (30%) + HOMO $\rightarrow$ LUMO+13 (22%) + HOMO $\rightarrow$ LUMO+10 (22%)) may be attributed to Ligand-to-Ligand CT. Low energy singlet band calculated in CH_2Cl_2 (325 nm) for complex **3**, arises primarily from HOMO $\rightarrow$ LUMO+10 (34%), HOMO $\rightarrow$ LUMO+4 (32%) and HOMO-3 $\rightarrow$ LUMO+2 (20%), which can also be assigned as 1 Ligand-to-Ligand Charge Transfer transitions.

The complexes **1-3** are non-emissive. The origin of ligand-mediated non-radiative decay of T_1 could lie in the non-radiative decay pathways for the T_1 excited states of the Pt(II) complexes **1-3**, which are promoted by symmetry breaking and ligand distortion. As shown in Figure 6, the ligand skeletons of complexes **1-3** in T_1 show large degrees of geometrical distortion relative to that of S_0 [48, 49]. For example in complex **1**, the dihedral angle P1-C7-C8-P4 increases by about 90° from S_0 to T_1 , accompanied by a 0.072 Å lengthening of the $\text{C}\equiv\text{C}$ bond. The other dihedral angle P2-C5-C6-P3 is reduced by 18° . The structural distortions from S_0 to T_1 are observed to occur to a lesser extent in **2** and **3** than in **1**.

Figure 6. DFT optimized S_0 and T_1 geometries for complexes **1-3**.

Conclusion

Reactivity of the complexes cis -[PtAr₂(SMe₂)₂](Ar = *p*-MeC₆H₄ and *p*-MeOC₆H₄) and cis,cis -[Me₂Pt(μ-SMe₂)₂PtMe₂] towards 1,1'-bis(diphenylphosphino)acetylene (dppac) were examined and new organoplatinum(II) complexes [Pt₂R₄(μ-dppac)₂], (R = Me, *p*-MeC₆H₄, *p*-MeOC₆H₄) have been obtained and characterized structurally and spectroscopically. In these dimeric complexes, dppac ligands are coordinated between two PtR₂ moieties in a

bridging mode *via* P-donor atoms. The UV-vis studies, supported by TD-DFT analysis, confirm a mixed ^1IL (intraligand charge transfer)/ $^1\text{MLCT}$ (metal-to-ligand charge transfer) when $\text{R} = \text{Me}$ and $^1\text{LLCT}$ (ligand-to-ligand charge transfer) for the complexes containing $\text{R} = p\text{-MeC}_6\text{H}_4$ and $p\text{-MeOC}_6\text{H}_4$.

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