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# A theoretical insight for solvent effect on myoglobin assay of $W(CO)_4L_2$ type novel complexes with DFT/TDDFT





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#### 1. Introduction

#### ABSTRACT

Novel tetracarbonyl complexes of type  $W(CO)_4L_2$  (L: 4-chlorobenzylimidazoline; 4methylbenzylimidazoline; 3,5-dimethylbenzylimidazoline; 2,4,6-trimethylbenzylimidazoline; 2,3,5,6tetramethylbenzylimidazoline) were synthesized. Then newly synthesized novel compounds were characterized by IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR and LC-MS. The characterizations of two of the complexes have also been confirmed with single crystal X-Ray diffraction and DFT optimization results of these complexes have been compared with single crystal results. We have investigated the solvent effect on the structure and metal-to-ligand charge transfer (MLCT) transitions with DFT/TDDFT calculations with ORCA package program with BP86 functional.

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Metal carbonyl complexes are important milestones in development of organometallic chemistry. Although early metal carbonyls were mostly used as catalyst [1], pharmaceutical applications of recent carbonyl complexes have accelerated the researches. Several practical applications of these complexes have been tested for probes in polymerization processes [2], labeling of biomolecules [3], and exploitation of solar energy [4]. The interest in these metal carbonyl complexes was reanimated after the recent publications by Motterlini et al. [5] who carried out CO-releasing properties of certain complexes of this family and this is the main subject of this manuscript.

Carbon monoxide (CO) is produced during the degradation of heme by the enzyme heme oxygenase [6,7], even though it is known as a toxic gas. The studies which shown the increment of the ratio of CO in case of illness [8–10] gave rise to new researches about bioactivity analyses of CO and have received considerable attention after the favorable results about functions of CO in tissue.

\* Corresponding author. E-mail address: elvanustun77@gmail.com (E. Üstün). Therefore, exogenous CO supplement is being accepted as an effective therapeutic way. Clinical trials using CO gas administered to patients by inhalation through the lungs are insecure for both the patients and the medical staff due to the inability to control delivery of CO [11]. Therefore, CO-releasing molecules (CORMs) became a reliable way out and metal carbonyl complexes are the most promising candidates for this mission [12–24]. There are various ways to ensure CO-release, one of which is to irradiate the complexes with UV-light with certain wavelength. These kinds of dark-stable and light-sensitive complexes are called as photo-CORMs [25–31].

Myoglobin assay is the most commonly used method for measuring CO-releasing properties of carbonyl complexes. It is principally based on following the transformation of deoxymyoglobin to carbonmonoxy-myoglobin by UV–Vis Spectrophotometer [5]. The photoCORMs have to be sensitive to certain wavelength of UV/Vis light but dark-stable in used solvent or solvent systems. Electronic transitions of molecules are the major landmark to make decision for proper wavelength of UV lamp. A photoCORM which has maxima on longer wavelength (preferably visible region) of UV spectra could be stimulated with a lower energy UV-lamp and is more advantageous for possible therapeutic applications [32]. Moreover, the darkstability and the electronic transitions of molecules depend on solvent. Therefore, it is important to have an insight about possible effect of solvents for reliable results and also to keep from waste of time, source, and labor.

The secondary ligands of CORMs have an influence on rate and amount of releasing CO and also solubility and stability of complexes. These ligands which also remain residual in tissue must be selected carefully. Furthermore, the well-selected ligands could strengthen the bioactivity synergistically. Imidazoline which is a prominent class of organic chemistry is an important bioactive molecule. Many imidazoline derivatives have been investigated as antihyperglycemic, antiinflammatory, antihypertensive, antihypercholesterolemic, and antidepressant reagents [33–39]. It should be also noted here that peripheral groups which can easily be substituted imidazoline changes the chemistry of both imidazoline and main organometallic compound.

Irradiation into the low-lying metal-to-ligand charge transfer (MLCT) bands, which belong to transitions from the metal to the lowest  $\pi^*$  orbital of the ligand, may give rise to photodissociation of carbonyl ligand and this is, in fact, the main mechanism of CO release with UV-light. An understanding of photochemistry of transition metal compounds requires knowledge of the properties of molecular orbitals, spectra and appropriate excited states. Density functional theory (DFT) and time-dependent DFT approach (TDDFT) plays a crucial role in characterization of the excited states coordination complexes [40–45]. Furthermore, applications of TDDFT approaches have recently been reported on transition metal complexes and got good results. Structures and electronic transitions predicted with the popular BP86 functional are no worse or in many cases are even slightly better than those predicted by the hybrid B3LYP functional [46–51].

The main objective of this study is to investigate the solvent effects on MLCT transitions of potential photoactivatable COreleasing molecules with theoretical methods. For this purpose, we synthesized novel tetracarbonyl complexes of type  $W(CO)_4L_2$  [L: 4-chlorobenzylimidazoline (L1), 4-methylbenzylimidazoline (L2), 3,5-dimethylbenzylimidazoline (L3), 2,4,6trimethylbenzylimidazoline (L4), 2,3,5,6tetramethylbenzylimidazoline (L5)]. The molecules were characterized by IR, 1H NMR, 13C NMR and LC-MS. The characterizations of two of the molecules have also been confirmed by single crystal X-Ray diffraction. DFT optimization results of these two complexes were also compared with the single crystal characteristics. The solvent effects on the structure and MLCT transitions have been investigated with DFT/TDDFT calculations using ORCA package program [41,46-48].

#### 2. Discussion

Imidazoline ligands (Fig. 1) were synthesized as in method of Çetinkaya et al. [52] with high yield (80–90%) and characterized. Although imidazole form of ligands were synthesized before and

even could be obtained commercially [53], imidazoline forms which were used in this study have not been encountered in any scientific papers. The most effective method for characterization -like many organic molecules-is <sup>1</sup>H NMR spectroscopy. Triplets for dorsal CH<sub>2</sub>-CH<sub>2</sub> part of imidazoline are characteristic and have come out between 2.85 and 3.82 ppm. Measured singlets between 6.70 and 7.03 ppm for NCHN and 3.98–4.12 ppm for elbow CH<sub>2</sub> connection of imidazoline-phenyl are also obvious evident. Additionally, the <sup>1</sup>H NMR signals for CH<sub>3</sub> on benzyl rings, <sup>13</sup>C NMR shifts and IR bands for all imidazoline ligands have been observed as expected. The characterization of ligands also have confirmed by elemental analysis.

Although only small changes are expected in <sup>1</sup>H NMR spectra of complexes, carbonyls' carbons could be observed in <sup>13</sup>C NMR. Three carbonyl shifts were recorded for **1** and **4** by chemical surrounding of carbonyl, but **2** and **3** had two signals while **5** had only a single one in 204.8 ppm. IR spectroscopy is a valuable method because of the unique bands of metal carbonyls and IR spectra of complexes have exhibited three absorption bands of the appropriate intensity pattern for the  $M(CO)_4$  fragment of  $C_{2V}$  local symmetry. The IR bands and LC-MS spectra of all complexes have confirmed the estimated structures.

The structures of **4** and **5** were additionally established by X-Ray structural analysis. The ORTEP drawing of **4** is shown in Fig. 2. Complexes **4** and **5** have distorted octahedral geometries and the imidazoline ligands were bonded to tungsten with *cis*-geometry. The crystallographic parameters of the molecules are given in Table 1.

The ORCA program package with the RI-BP86 and a TZV basis set were used for theoretical geometry optimization of all complexes. Some calculated bond lengths and angles of **4** and **5** have been compared with single crystal X-Ray results (Table 2). The deviations between calculated bond lengths and those obtained by crystallography have been recorded in  $\pm 0.02$  Å, while bond angle deviations do not exceed 2.1%, in absolute terms, less than 3.85°. These results mean that ORCA package with these functionals could be used for calculation of structural parameters of all this kind of molecules, so the Cartesian coordinates of all studied molecules were given in Supporting Information part for possible further studies.

UV–Vis spectroscopy is major for in-vitro bioactivity studies of organometallic compounds (i.e., antioxidant activity, CO-releasing activity), but the spectra of compounds are appraised negligible because of generally used indirect measurement methods. However, each compound has differences with regard to stability and UV bands in different solvents and this is an important deficiency of methods which irradiation used in. In this study, we especially wanted to have an insight about the solvent effects on photo-CORMs; because the reliable wavelength in CO-releasing analyzing process is selected according to UV–Vis maxima of molecule which depends on the solvent used. The complex **1** displayed maxima on 321 nm in DMSO and on 288 nm in acetonitrile while complex **3** 

	Positions					
	Ligand	2	3	4	5	6
6, 5	L1	Н	Н	Cl	Н	Н
	L2	Н	Н	CH <sub>3</sub>	Н	Н
	L3	Н	CH <sub>3</sub>	Н	CH <sub>3</sub>	Н
$\left[ \right]^{N} \left[ \right]^{2} \left[ \right]^{3}$	L4	CH <sub>3</sub>	Н	CH <sub>3</sub>	Н	CH <sub>3</sub>
	L5	CH <sub>3</sub>	CH <sub>3</sub>	Н	CH <sub>3</sub>	CH <sub>3</sub>

Fig. 1. Imidazoline derivative ligands of type W(CO)<sub>4</sub>L<sub>2</sub> complexes.



Fig. 2. An ORTEP drawing of 4 with the atomic numbering scheme.

Table 1Crystallographic parameters of 4 and 5.

$\begin{array}{llllllllllllllllllllllllllllllllllll$		4	5
$\begin{array}{lll} \mbox{Formula weight} & 700.49 & 728.53 \\ \mbox{Dimensions (mm)} & 0.539 \times 0.324 \times 0.184 & 0.44 \times 0.39 \times 0.16 \\ \mbox{Crystal system} & Monoclinic & Monoclinic \\ \mbox{Space group} & C 12/c1 & P2 1/c \\ a (Å) & 14.8659 (8) & 8.9422 (3) \\ b (Å) & 9.0291 (4) & 19.1742 (6) \\ c (Å) & 23.1920 (11) & 18.5366 (7) \\ \alpha (°) & 90 & 90 \\ \beta (°) & 105.455 (1) & 92.474 (3) \\ \gamma (°) & 90 & 90 \\ \gamma (°) & 90 & 90 \\ \gamma (°) & 90 & 90 \\ \gamma (°) & 90 & 105.455 (1) \\ Z & 4 & 4 \\ \rho_{calc} (g  cm^{-3}) & 1.5506 & 1.524 \\ T (K) & 100 & 296 \\ \mu (mm^{-1}) & 3.889 & 3.68 \\ \lambda (Å) (Mo K_z) & 0.71073 & 0.71073 \\ 2\Theta_{max} (°) & 28.29 & 27.1 \\ \mbox{Reflection measured} & 16190 & 20751 \\ \mbox{Unique refl.}[(1 \ge 2u(1)] & 3733/3578 & 7001/5236 \\ \mbox{Variables} & 179 & 371 \\ R (I> = 2u(I)) & 0.0352 & 0.084 \\ \mbox{Largest different map} & 0.4876/-1.2653 & 1.04/-1.31 \\ \mbox{peak/obe in e Å}^3- \\ \end{array}$	Empirical Formula	C <sub>30</sub> H <sub>36</sub> N <sub>4</sub> O <sub>4</sub> W	C32H40N4O4W
$\begin{array}{lll} \mbox{Dimensions (mm)} & 0.539 \times 0.324 \times 0.184 & 0.44 \times 0.39 \times 0.16\\ \mbox{Crystal system} & \mbox{Monoclinic} & \mbox{Monoclinic} \\ \mbox{Space group} & C 12/c1 & P2 1/c \\ a (Å) & 14.8659 (8) & 8.9422 (3) \\ b (Å) & 9.0291 (4) & 19.1742 (6) \\ c (Å) & 23.1920 (11) & 18.5366 (7) \\ \alpha (^{\circ}) & 90 & 90 \\ \beta (^{\circ}) & 105.455 (1) & 92.474 (3) \\ \gamma (^{\circ}) & 90 & 90 \\ V (Å^3) & 3000.4 (3) & 3175.31 (19) \\ Z & 4 & 4 \\ \rho_{calc} (g  cm^{-3}) & 1.5506 & 1.524 \\ T (K) & 100 & 296 \\ \mu (mm^{-1}) & 3.889 & 3.68 \\ \lambda (Å) (Mo K_z) & 0.71073 & 0.71073 \\ 2\Theta_{max} (^{\circ}) & 28.29 & 27.1 \\ Reflection measured & 16190 & 20751 \\ Unique refl./[(1 \ge 2u(1)] & 3733/3578 & 7001/5236 \\ Variables & 179 & 371 \\ R (I> = 2u(I)) & 0.0157 & 0.066 \\ w R (I> = 2u(I)) & 0.0352 & 0.084 \\ Largest different map & 0.4876/-1.2653 & 1.04/-1.31 \\ peak/hole in e Å^3^- \\ \end{array}$	Formula weight	700.49	728.53
$\begin{array}{llllllllllllllllllllllllllllllllllll$	Dimensions (mm)	$0.539\times0.324\times0.184$	$0.44 \times 0.39 \times 0.16$
Space groupC 12/c1P2 1/c $a$ (Å)14.8659 (8)8.9422 (3) $b$ (Å)9.0291 (4)19.1742 (6) $c$ (Å)23.1920 (11)18.5366 (7) $\alpha$ (°)9090 $\beta$ (°)105.455 (1)92.474 (3) $\gamma$ (°)9090 $V$ (Å3)3000.4 (3)3175.31 (19) $Z$ 44 $\rho_{calc}$ (g cm <sup>-3</sup> )1.55061.524 $T$ (K)100296 $\mu$ (mm <sup>-1</sup> )3.8893.68 $\lambda$ (Å) (Mo K $_2$ )0.710730.71073 $2\Theta_{max}$ (°)28.2927.1Reflection measured1619020751Unique refl./[(1 $\ge$ 2u(1)]3733/35787001/5236Variables179371 $R$ ( $l> = 2u(I)$ )0.03520.084Largest different map0.4876/-1.26531.04/-1.31peak/hole in e Å <sup>3-</sup>	Crystal system	Monoclinic	Monoclinic
a (Å)14.8659 (8)8.9422 (3)b (Å)9.0291 (4)19.1742 (6)c (Å)23.1920 (11)18.5366 (7) $\alpha$ (°)9090 $\beta$ (°)105.455 (1)92.474 (3) $\gamma$ (°)9090V (Å3)3000.4 (3)3175.31 (19)Z44 $\rho_{calc}$ (g cm <sup>-3</sup> )1.55061.524T (K)100296 $\mu$ (mm <sup>-1</sup> )3.8893.68 $\lambda$ (Å) (Mo K <sub>2</sub> )0.710730.710732 $\Theta_{max}$ (°)28.2927.1Reflection measured1619020751Unique refl./[(1 ≥ 2u(1)]3733/35787001/5236Variables179371 $R$ ( $b = 2u(I)$ )0.03520.084Largest different map0.4876/-1.26531.04/-1.31peak/hole in e Å <sup>3-</sup> -	Space group	C 12/c1	P2 1/c
$\begin{array}{lll} b\left(\dot{A}\right) & 9.0291 \left(4\right) & 19.1742 \left(6\right) \\ c\left(\dot{A}\right) & 23.1920 \left(11\right) & 18.5366 \left(7\right) \\ \alpha\left(^{\circ}\right) & 90 & 90 \\ \beta\left(^{\circ}\right) & 105.455 \left(1\right) & 92.474 \left(3\right) \\ \gamma\left(^{\circ}\right) & 90 & 90 \\ V\left(\dot{A}^3\right) & 3000.4 \left(3\right) & 3175.31 \left(19\right) \\ Z & 4 & 4 \\ \rho_{calc} \left(g  cm^{-3}\right) & 1.5506 & 1.524 \\ T\left(K\right) & 100 & 296 \\ \mu\left(mm^{-1}\right) & 3.889 & 3.68 \\ \lambda\left(\dot{A}\right) \left(Mo  K_z\right) & 0.71073 & 0.71073 \\ 2\Theta_{max} \left(^{\circ}\right) & 28.29 & 27.1 \\ Reflection measured & 16190 & 20751 \\ Unique refl./[(1 \ge 2u(1)] & 3733/3578 & 7001/5236 \\ Variables & 179 & 371 \\ R\left(l> = 2u(l)\right) & 0.0157 & 0.066 \\ wR\left(l> = 2u(l)\right) & 0.0352 & 0.084 \\ Largest different map & 0.4876/-1.2653 & 1.04/-1.31 \\ peak/hole in e  \dot{A}^{3-} \end{array}$	a (Å)	14.8659 (8)	8.9422 (3)
$\begin{array}{cccc} c(\bar{A}) & 23.1920 (11) & 18.5366 (7) \\ \alpha(^{\circ}) & 90 & 90 \\ \beta(^{\circ}) & 105.455 (1) & 92.474 (3) \\ \gamma(^{\circ}) & 90 & 90 \\ V(\bar{A}^3) & 3000.4 (3) & 3175.31 (19) \\ Z & 4 & 4 \\ \rho_{calc}(gcm^{-3}) & 1.5506 & 1.524 \\ T(\bar{K}) & 100 & 296 \\ \mu(mm^{-1}) & 3.889 & 3.68 \\ \lambda(\bar{A})(\bord{Mo}K_2) & 0.71073 & 0.71073 \\ 2\Theta_{max}(^{\circ}) & 28.29 & 27.1 \\ Reflection measured & 16190 & 20751 \\ Unique\ refl./[(1 \ge 2u(1)] & 3733/3578 & 7001/5236 \\ Variables & 179 & 371 \\ R(l>= 2u(l)) & 0.0157 & 0.066 \\ wR(l>= 2u(l)) & 0.0352 & 0.084 \\ Largest different map & 0.4876/-1.2653 & 1.04/-1.31 \\ peak/hole in e\ A^{3-} \end{array}$	b (Å)	9.0291 (4)	19.1742 (6)
$\begin{array}{lll} \alpha \left( \stackrel{\circ}{\circ} \right) & 90 & 90 \\ \beta \left( \stackrel{\circ}{\circ} \right) & 105.455 \left( 1 \right) & 92.474 \left( 3 \right) \\ \gamma \left( \stackrel{\circ}{\circ} \right) & 90 & 90 \\ V \left( \stackrel{A}{3} \right) & 3000.4 \left( 3 \right) & 3175.31 \left( 19 \right) \\ Z & 4 & 4 \\ \rho_{calc} \left( g  cm^{-3} \right) & 1.5506 & 1.524 \\ T \left( K \right) & 100 & 296 \\ \mu \left( mm^{-1} \right) & 3.889 & 3.68 \\ \lambda \left( \stackrel{A}{\Lambda} \left( Mo  K_z \right) & 0.71073 & 0.71073 \\ 2\Theta_{max} \left( \stackrel{\circ}{\circ} \right) & 28.29 & 27.1 \\ Reflection measured & 16190 & 20751 \\ Unique refl./[(1 \ge 2u(1)] & 3733/3578 & 7001/5236 \\ Variables & 179 & 371 \\ R \left( l^{>} = 2u(l) \right) & 0.0157 & 0.066 \\ w R \left( l^{>} = 2u(l) \right) & 0.352 & 0.084 \\ Largest different map & 0.4876/-1.2653 & 1.04/-1.31 \\ peak/hole in e  A^{3-} \end{array}$	c (Å)	23.1920 (11)	18.5366 (7)
$\begin{array}{lll} \beta\left( ^{\circ}\right) & 105.455\left( 1\right) & 92.474\left( 3\right) \\ 90 & 90 \\ V\left( ^{3}\right) & 3000.4\left( 3\right) & 3175.31\left( 19\right) \\ Z & 4 & 4 \\ \rho_{calc}\left( gcm^{-3}\right) & 1.5506 & 1.524 \\ T\left( K\right) & 100 & 296 \\ \mu\left( mm^{-1}\right) & 3.889 & 3.68 \\ \lambda\left( \tilde{A}\right) \left( MoK_{z}\right) & 0.71073 & 0.71073 \\ 2\Theta_{max}\left( ^{\circ}\right) & 28.29 & 27.1 \\ Reflection measured & 16190 & 20751 \\ Unique refl./[(1 \ge 2u(1)] & 3733/3578 & 7001/5236 \\ Variables & 179 & 371 \\ R\left( l>= 2u(l) \right) & 0.0157 & 0.066 \\ wR\left( l>= 2u(l) \right) & 0.0352 & 0.084 \\ Largest different map & 0.4876/-1.2653 & 1.04/-1.31 \\ peak/hole in e Å^{3-} \end{array}$	α (°)	90	90
$\begin{array}{lll} \gamma\left( \stackrel{\circ}{\circ} \right) & 90 & 90 \\ V\left( \stackrel{A}{A} \right) & 3000.4 \left( 3 \right) & 3175.31 \left( 19 \right) \\ Z & 4 & 4 \\ \rho_{calc} \left( g  cm^{-3} \right) & 1.5506 & 1.524 \\ T\left( K \right) & 100 & 296 \\ \mu \left( mm^{-1} \right) & 3.889 & 3.68 \\ \lambda \left( \stackrel{A}{A} \right) \left( Mo  K_z \right) & 0.71073 & 0.71073 \\ 2\Theta_{max} \left( \stackrel{\circ}{\circ} \right) & 28.29 & 27.1 \\ \text{Reflection measured} & 16190 & 20751 \\ \text{Unique refl.} \left[ \left[ 1 \ge 2u(1) \right] & 3733/3578 & 7001/5236 \\ \text{Variables} & 179 & 371 \\ R \left( I_{>} = 2u(I) \right) & 0.0157 & 0.066 \\ wR \left( I_{>} = 2u(I) \right) & 0.0352 & 0.084 \\ \text{Largest different map} & 0.4876/-1.2653 & 1.04/-1.31 \\ \text{peak/hole in e $A^{3-} \end{array}$	β(°)	105.455 (1)	92.474 (3)
$\begin{array}{lll} V(\Bar{A}^3) & 3000.4(3) & 3175.31(19) \\ Z & 4 & 4 \\ \rho_{calc}(gcm^{-3}) & 1.5506 & 1.524 \\ T(K) & 100 & 296 \\ \mu(mm^{-1}) & 3.889 & 3.68 \\ \lambda(\Bar{A})(MoK_{\alpha}) & 0.71073 & 0.71073 \\ 2\Theta_{max}(^\circ) & 28.29 & 27.1 \\ Reflection measured & 16190 & 20751 \\ Unique refl./[(1 \ge 2u(1)] & 3733/3578 & 7001/5236 \\ Variables & 179 & 371 \\ R(l>= 2u(l)) & 0.0157 & 0.066 \\ wR(l>= 2u(l)) & 0.0352 & 0.084 \\ Largest different map & 0.4876/-1.2653 & 1.04/-1.31 \\ peak/hole in e\Bar{A}^{3-} \end{array}$	γ (°)	90	90
$\begin{array}{cccc} Z & 4 & 4 \\ \rho_{calc} \left( g  cm^{-3} \right) & 1.5506 & 1.524 \\ T \left( K \right) & 100 & 296 \\ \mu \left( mm^{-1} \right) & 3.889 & 3.68 \\ \lambda \left( \dot{A} \right) \left( Mo  K_{z} \right) & 0.71073 & 0.71073 \\ 2\Theta_{max} \left( ^{\circ} \right) & 28.29 & 27.1 \\ Reflection measured & 16190 & 20751 \\ Unique refl./[(1 \ge 2u(1)] & 3733/3578 & 7001/5236 \\ Variables & 179 & 371 \\ R \left( l > 2u(l) \right) & 0.0157 & 0.066 \\ wR \left( l > 2u(l) \right) & 0.0352 & 0.084 \\ Largest different map & 0.4876/-1.2653 & 1.04/-1.31 \\ peak/hole in e Å^{3-} \end{array}$	V (Å <sup>3</sup> )	3000.4 (3)	3175.31 (19)
$\begin{array}{lll} \rho_{calc} (g\ cm^{-3}) & 1.5506 & 1.524 \\ T\ (K) & 100 & 296 \\ \mu\ (mm^{-1}) & 3.889 & 3.68 \\ \lambda\ (Å)\ (Mo\ K_z) & 0.71073 & 0.71073 \\ 2\Theta_{max} (^\circ) & 28.29 & 27.1 \\ Reflection\ measured & 16190 & 20751 \\ Unique\ refl./[(1 \geq 2u(1)] & 3733/3578 & 7001/5236 \\ Variables & 179 & 371 \\ R\ (l>= 2u(l)) & 0.0157 & 0.066 \\ wR\ (l>= 2u(l)) & 0.0352 & 0.084 \\ Largest\ different\ map & 0.4876/-1.2653 & 1.04/-1.31 \\ peak/hole\ in\ e\ A^{3-} \end{array}$	Ζ	4	4
$\begin{array}{llllllllllllllllllllllllllllllllllll$	$\rho_{calc} (g \text{ cm}^{-3})$	1.5506	1.524
$\begin{array}{lll} \mu \ (mm^{-1}) & 3.889 & 3.68 \\ \lambda \ (\begin{tabular}{lll} \lambda \ (\begin{tabular}{lll} M \ \end{tabular} K_z) & 0.71073 & 0.71073 \\ 2\Theta_{max} \ (^\circ) & 28.29 & 27.1 \\ Reflection measured & 16190 & 20751 \\ Unique \ refl./[(1 \ge 2u(1)] & 3733/3578 & 7001/5236 \\ Variables & 179 & 371 \\ R \ (l>= 2u(l)) & 0.0157 & 0.066 \\ wR \ (l>= 2u(l)) & 0.0352 & 0.084 \\ Largest \ different \ map & 0.4876/-1.2653 & 1.04/-1.31 \\ peak/hole \ in \ e \ A^{3-} \end{array}$	T (K)	100	296
$\begin{array}{lll} \lambda\left(\dot{A}\right) (Mo \ K_z) & 0.71073 & 0.71073 \\ 2\Theta_{max}\left(^{\circ}\right) & 28.29 & 27.1 \\ Reflection measured & 16190 & 20751 \\ Unique \ refl./[(1 \ge 2u(1)] & 3733/3578 & 7001/5236 \\ Variables & 179 & 371 \\ R \ (l> = 2u(l)) & 0.0157 & 0.066 \\ wR \ (l> = 2u(l)) & 0.0352 & 0.084 \\ Largest \ different \ map & 0.4876/-1.2653 & 1.04/-1.31 \\ peak/hole \ in \ e \ A^{3-} \end{array}$	$\mu$ (mm <sup>-1</sup> )	3.889	3.68
$\begin{array}{llllllllllllllllllllllllllllllllllll$	λ (Å) (Mo K <sub>α</sub> )	0.71073	0.71073
Reflection measured         16190         20751           Unique refl./[( $l \ge 2u(l)$ ]         3733/3578         7001/5236           Variables         179         371 $R$ ( $l > 2u(l)$ )         0.0157         0.066           wR ( $l > 2u(l)$ )         0.0352         0.084           Largest different map         0.4876/-1.2653         1.04/-1.31           peak/hole in e Å <sup>3-</sup> 37-	$2\Theta_{\max}$ (°)	28.29	27.1
Unique refl./[( $l \ge 2u(1)$ ]       3733/3578       7001/5236         Variables       179       371 $R$ ( $l > 2u(l)$ )       0.0157       0.066         wR ( $l > 2u(l)$ )       0.0352       0.084         Largest different map       0.4876/-1.2653       1.04/-1.31         peak/hole in e Å <sup>3-</sup> 7	Reflection measured	16190	20751
Variables         179         371 $R$ ( $I> = 2u(I)$ )         0.0157         0.066           wR ( $I> = 2u(I)$ )         0.0352         0.084           Largest different map         0.4876/-1.2653         1.04/-1.31           peak/hole in e Å <sup>3-</sup> 7	Unique refl./[ $(I \ge 2u(I)]$	3733/3578	7001/5236
R ( $I > = 2u(I)$ )       0.0157       0.066         wR ( $I > = 2u(I)$ )       0.0352       0.084         Largest different map       0.4876/-1.2653       1.04/-1.31         peak/hole in e Å <sup>3-</sup> 0.4876/-1.2653       0.04/-1.31	Variables	179	371
wR ( $I> = 2u(I)$ )       0.0352       0.084         Largest different map       0.4876/-1.2653       1.04/-1.31         peak/hole in e Å <sup>3-</sup> 0.4876/-1.2653       0.04/-1.31	R(I > = 2u(I))	0.0157	0.066
Largest different map 0.4876/-1.2653 1.04/-1.31 peak/hole in e Å <sup>3-</sup>	wR(I > = 2u(I))	0.0352	0.084
peak/hole in e Å <sup>3-</sup>	Largest different map	0.4876/-1.2653	1.04/-1.31
	peak/hole in e Å <sup>3-</sup>		

Table 2Selected experimental and calculatedb molecular parameters (bond lengths andangles) for 4 and 5 in gas phasea.

	4		5		
	Experimental	Theoretical	Experimental	Theoretical	
W1-C1	2.03(19)	2.02	2.01(6)	2.02	
W1-C2	1.95(19)	1.96	1.96(5)	1.96	
C1-01	1.15(2)	1.20	1.17(7)	1.20	
C2-02	1.17(2)	1.20	1.16(6)	1.20	
W1-N1	2.23(15)	2.23	2.24(3)	2.24	
N1-C3	1.29(2)	1.32	1.29(5)	1.32	
N2-C6	1.46(2)	1.48	1.45(6)	1.48	
C6–C7	1.51(3)	1.52	1.52(7)	1.52	
C1-W1-C2	86.31(7)	85.95	87.80(2)	86.31	
C1–W1–C1 <sup>i</sup>	171.64(11)	171.06	169.00(2)	167.07	
N1-W1-N1 <sup>i</sup>	80.18(8)	84.03	81.44(14)	84.20	
N1-W1-C1	92.39(6)	92.20	96.06(19)	94.00	
N1-W1-C2	176.37(7)	176.16	177.62(16)	175.70	
W1-C1-01	176.83(17)	178.14	171.50(5)	170.90	
N1-C3-N2	116.81(16)	116.18	117.50(4)	116.30	
N2-C6-C7	112.67(15)	113.60	112.40(4)	113.80	

<sup>a</sup> Bond lengths in Angstrom and bond angles in degrees.

<sup>b</sup> Computed at the RI-BP86/TZV (ZORA) level of theory.

had maxima on 320 nm in DMSO, on 296 nm in toluene, and on 253 nm in ethyl acetate (Fig. 3a, Table S1). On the other hand, the darkstability of the molecules in different solvents changes the CO-releasing capacity and this could be a shadow on reliability of experiments and used method (Fig. 3b). There are some restrictions on the choice of solvents in biochemical texts [54,55] and it is obvious that CO-releasing analysis process of photoCORMs must be evaluated according to solvent alteration.

All five molecules were structurally optimized by DFT with ORCA package taking into account eight different organic solvents (acetonitrile, carbon tetrachloride, dimethylformamide, hexane, methanol, tetrahydrofuran, toluene and, water) with COSMO model and some bond lengths and angles of **4** were compared with each other in Table 3. Tungsten compounds containing aromatic ligands usually exhibit intense metal-to-ligand charge transfer (MLCT) transitions in UV–Vis spectrum. Electronic transitions and contributor molecular orbitals were analyzed firstly with the aim of providing the participation to spectra bands in different solvents. Only strong transitions with an oscillator strength >0.01 are

reported and contributions >20% are listed in tables. In methanol, HOMO of molecule intensively consists of transition metal orbitals while LUMO is formed completely from carbonyl orbitals, thus the HOMO-LUMO transition is a kind of MLCT which is expected to occur in 570.6 nm theoretically, but this transition could not be observed in UV-spectra practically because of weak oscillation strength. Electronic states with highest oscillating force are state 24 and state 31 in which electrons flow from metal to imidazoline and these states mostly include HOMO-1  $\rightarrow$  LUMO + 7 and HOMO-1  $\rightarrow$  LUMO + 8, respectively (Table 4). However, the highest oscillator transition of the same molecule in hexane consists of electron flow completely from carbonyl to imidazoline and is entirely independent from tungsten atom (Table 5). Electronic transition analyses for all five molecules in hexane, methanol and DMF could be also seen in Supporting Information files.

The MLCT energies are very sensitive to the nature of solvent. The wavelength of MLCT absorption depends on solvent type in addition to solvent polarity. We also analyzed how the solvent affected the HOMO-LUMO transition energy and the energy levels of frontier orbitals (Fig. 4). The molecule **2** was analyzed exemplary, there were no clear differences between energy levels in gas phase and in hexane, but acetonitrile evidently reduced the energies of frontier orbitals. HOMO-LUMO energy gap was evaluated for



Fig. 3. Solvent effects on UV-Vis spectra (a) and darkstability (b) of 3.

#### Table 3

Comparison of calculated<sup>b</sup> selected bond lengths and angles<sup>a</sup> for **4** in different solvents with experimental values from X-ray analysis.

	Exp.	CCl <sub>4</sub>	MeOH	Acetonitrile
W1-C1	2.03(19)	2.017	2.017	2.017
W1-C2	1.95(19)	1.958	1.955	1.955
C101	1.15(2)	1.200	1.202	1.201
C2-02	1.17(2)	1.206	1.212	1.212
W1-N1	2.23(15)	2.233	2.221	2.220
N1-C3	1.29(2)	1.323	1.326	1.327
N2-C6	1.46(2)	1.478	1.480	1.480
C6-C7	1.51(3)	1.518	1.518	1.518
C1-W1-C2	86.31(7)	84.9	84.5	84.1
C1–W1–C1 <sup>i</sup>	171.64(11)	166.2	163.9	163.9
N1-W1-N1 <sup>i</sup>	80.18(8)	82.8	82.0	82.0
N1-W1-C1	92.39(6)	95.2	96.1	96.0
W1-C1-O1	176.83(17)	170.2	168.1	168.1
N1-C3-N2	116.81(16)	116.1	116.1	116.1
N2-C6-C7	112.67(15)	113.6	113.6	113.6

<sup>a</sup> Bond lengths in Angstrom and bond angles in degrees.

<sup>b</sup> Computed at the RI-BP86/TZV (ZORA)/COSMO level of theory.

molecule **2**, and also for all molecules in all eight solvents in this study. In fact, we could not see a meaningful relation depending on solvents, dipole moments, and dielectric constants; but there are lots of theoretical studies for catching an equation between a molecular parameter and HOMO-LUMO transition energy and our calculation results were added to Supporting Information for possible further studies of other groups (Table S16).

#### 3. Conclusion

We have synthesized four novel tungsten carbonyl complexes of type W(CO)<sub>4</sub>L<sub>2</sub> with imidazoline derivative ligands. These compounds were fully characterized by spectroscopic methods. We have investigated frontier molecular orbitals, electronic transitions, and singlet excitation density differences of the compounds by using DFT/TDDFT methods. The results confirm that increment of  $\pi$ -back bonding leads to deceleration of CO release and the ancillary ligands play remarkable role in the W-CO bond labialization process.

#### 4. Material and method

#### 4.1. General remarks

All chemicals were purchased from Sigma Aldrich and used

without further purification. All reactions were carried out under an atmosphere of pure argon by using standard Schlenk and vacuum techniques. Solvents were freshly distilled after refluxing over metallic sodium or phosphorous pentoxide for 3–4 days. IR spectra were recorded on pure solid samples with a Shimadzu IRAffinity-1 ATR spectrometer. Intensities of stretching vibrations were marked as strong(s), medium (m), weak (w), or shoulder (sh). NMR spectra were recorded on a Bruker Ultra Shield 300 MHz spectrometer. Chemical shifts  $\delta$  in parts per million indicate a downfield shift relative to tetramethylsilane (TMS) and were referenced relative to the signal of the solvents. Coupling constants J are given in hertz. Individual peaks are marked as singlet (s), doublet (d), triplet (t), or multiplet (m). Absorption spectra were measured using a Shimadzu UV-1800 in quartz cuvettes (d = 1 cm). Elemental analysis (C, H, and N) of ligands was carried out using a CHNS-932 (LECO).

#### 4.2. Synthesis of ligands

All ligands were prepared by similar methods. Small pieces of lithium (45 mmol, 312 mg) were added slowly to ethylene diamine at 110 °C. The solution was allowed to reach room temperature after stirring for 1 h and *n*-alkylbenzylchloride (50 mmol) and toluene (40 mL) were added. Precipitated lithium chloride was filtered and the N-(*n*-alkylbenzyl)ethylenediamine was isolated by distillation from the oily mixture (120 °C/0.01 mmHg) after solvents were removed under vacuum. N-(*n*-alkylbenzyl)ethylenediamine (35 mmol) and N,N-dimethylformamide dimethylacetal (40 mmol) were stirred for 2 h at 100 °C and methanol and dimethyl amine were separated at 120 °C by distillation. The last product was isolated from yellow oily residue by distillation under vacuum (124 °C/ 0.01 mmHg).

#### 4.2.1. N-4-chlorobenzylimidazoline [L1]

<sup>1</sup>H NMR ( $\delta$ , 300 MHz, CDCl<sub>3</sub>): 3.03 (t, 2H, J = 9.75 Hz, NCH<sub>2</sub>CH<sub>2</sub>N), 3.76 (t, 2H, J = 9.78 NCH<sub>2</sub>CH<sub>2</sub>N), 4.18 (s, 2H, NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Cl-4), 7.14 and 7.25 (d, J = 8.4 Hz, 4H, NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Cl-4), 6.89 (s, 1H, NCHN). <sup>13</sup>C NMR ( $\delta$ , 75 MHz, CDCl<sub>3</sub>): 48.1 and 51.1(NCH<sub>2</sub>CH<sub>2</sub>N), 55.2 (NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Cl-4), 128.8, 129.1, 133.3 and 135.6 (NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Cl-4), 157.3 (NCHN). Anal. Calc. for C<sub>11</sub>H<sub>14</sub>N<sub>2</sub>Cl (194.06): C, 61.70; H, 5.70; N, 14.39. Found: C, 61.68; H, 5.73; N, 14.38%.

#### 4.2.2. N-4-methylbenzylimidazoline [L2]

<sup>1</sup>H NMR ( $\delta$ , 300 MHz, CDCl<sub>3</sub>): 2.13 (s, 3H, NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>)-4), 3.98 (s, 2H, NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>)-4), 6.90-6.93 (m, 4H, NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>)-

#### Table 4

Energies (in nm), Oscillator Strength (f<sub>osc</sub>), Main Orbital Contributions, and Type of Transition Involved in the Most Important Singlet Excitations for **3** in Methanol Calculated with TDDFT/BP86.



4), 2.85 and 3.58 (t, J = 9.8 Hz, 4H, NCH<sub>2</sub>CH<sub>2</sub>N), 6.70 (s, 1H, NCHN). <sup>13</sup>C NMR ( $\delta$ , 75 MHz, CDCl<sub>3</sub>): 21.11 (NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>)-4), 55.18 (NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>)-4), 127.76, 128.23, 129.03, 129.37, 133.93, 137.33 (NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>)-4), 50.03 and 51.46 (NCH<sub>2</sub>CH<sub>2</sub>N), 157.52 (NCHN). Anal. Calc. for C<sub>11</sub>H<sub>14</sub>N<sub>2</sub> (174.12): C, 75.82; H, 8.10; N, 16.08. Found: C, 75.83; H, 8.08; N, 16.06%.

#### 4.2.3. N-3,5-dimetylbenzylimidazoline [L3]

<sup>1</sup>H NMR ( $\delta$ , 300 MHz, CDCl<sub>3</sub>): 2.30 and 2.40 (s, 6H, 3,5-CH<sub>2</sub>C<sub>6</sub>H<sub>3</sub>(CH<sub>3</sub>)<sub>2</sub>), 4.12 (s, 2H, 3,5-CH<sub>2</sub>C<sub>6</sub>H<sub>3</sub>(CH<sub>3</sub>)<sub>2</sub>), 6.72 (s, 2H, 3,5-CH<sub>2</sub>C<sub>6</sub>H<sub>3</sub>(CH<sub>3</sub>)<sub>2</sub>), 6.81 (s, 1H, 3,5-CH<sub>2</sub>C<sub>6</sub>H<sub>3</sub>(CH<sub>3</sub>)<sub>2</sub>), 3.11 and 3.58 (t, *J* = 9.6 Hz, 4H, NCH<sub>2</sub>CH<sub>2</sub>N), 7.03 (s, 1H, NCHN). <sup>13</sup>C NMR ( $\delta$ , 75 MHz, CDCl<sub>3</sub>): 20.03 (3,5-CH<sub>2</sub>C<sub>6</sub>H<sub>3</sub>(CH<sub>3</sub>)<sub>2</sub>), 45.3, 49.0 (NCH<sub>2</sub>CH<sub>2</sub>N), 52.4

#### Table 5

Energies (in nm), Oscillator Strength ( $f_{osc}$ ), Main Orbital Contributions, and Type of Transition Involved in the Most Important Singlet Excitations for **3** in Hexane Calculated with TDDFT/BP86.

State	λ/nm	f <sub>osc</sub>	Main transitions	Type of transitions
1	560.9	0.0165	166 → 167 (95.6%)	$W/CO \rightarrow CO (MLCT/LLCT)$
8	447.9	0.0437	166 → 171 (25.3%)	W/CO $\rightarrow$ imid (MLCT/LLCT)
			166 → 173 (53.4%)	W/CO $\rightarrow$ imid (MLCT/LLCT)
9	447.7	0.0329	166 → 174 (69.7%)	W/CO $\rightarrow$ imid (MLCT/LLCT)
13	427.0	0.0316	165 → 171 (73.5%)	W/CO $\rightarrow$ imid (MLCT/LLCT)
19	415.9	0.0121	165 → 173 (91.2%)	W/CO $\rightarrow$ imid (MLCT/LLCT)
21	386.1	0.0198	165 → 174 (76.4%)	W/CO $\rightarrow$ imid (MLCT/LLCT)
22	390.3	0.0110	164 → 173 (86.7%)	W/CO $\rightarrow$ imid (MLCT/LLCT)
30	316.7	0.0453	163 → 168 (74.4%)	imid $\rightarrow$ CO (LLCT)
39	287.6	0.0155	162 → 168 (38.7%)	imid $\rightarrow$ CO (LLCT)
			$165 \to 176~(24.6\%)$	imid $\rightarrow$ CO (LLCT)

 $(3,5-CH_2C_6H_3(CH_3)_2), 127.2, 128.8, 136.4, 137.8 (3,5-CH_2C_6H_3(CH_3)_2), 157.8 (NCHN).$  Anal. Calc. for C<sub>12</sub>H<sub>16</sub>N<sub>2</sub> (188.13): C, 76.55; H, 8.57; N, 14.88. Found: C, 76.53; H, 8.59; N, 14.87%.

#### 4.2.4. N-2,4,6-trimetylbenzylimidazoline [L4]

<sup>1</sup>H NMR ( $\delta$ , 300 MHz, CDCl<sub>3</sub>): 2.29 and 2.42 (s, 9H, 2,4,6-CH<sub>2</sub>C<sub>6</sub>H<sub>2</sub>(CH<sub>3</sub>)<sub>3</sub>), 4.17 (s, 2H, 2,4,6-CH<sub>2</sub>C<sub>6</sub>H<sub>2</sub>(CH<sub>3</sub>)<sub>3</sub>), 6.84 (s, 2H, 2,4,6-CH<sub>2</sub>C<sub>6</sub>H<sub>2</sub>(CH<sub>3</sub>)<sub>3</sub>), 3.14 and 3.74 (t, *J* = 9.6 Hz, 4H, NCH<sub>2</sub>CH<sub>2</sub>N), 6.97 (s, 1H, NCHN). <sup>13</sup>C NMR ( $\delta$ , 75 MHz, CDCl<sub>3</sub>): 19.9 and 21.1 (2,4,6-CH<sub>2</sub>C<sub>6</sub>H<sub>2</sub>(CH<sub>3</sub>)<sub>3</sub>), 45.7, 49.1 (NCH<sub>2</sub>CH<sub>2</sub>N), 55.2 (2,4,6-CH<sub>2</sub>C<sub>6</sub>H<sub>2</sub>(CH<sub>3</sub>)<sub>3</sub>), 129.5, 129.8, 137.5, 137.6 (2,4,6-CH<sub>2</sub>C<sub>6</sub>H<sub>2</sub>(CH<sub>3</sub>)<sub>3</sub>), 156.8 (NCHN). Anal. Calc. for C<sub>13</sub>H<sub>18</sub>N<sub>2</sub> (202.15): C, 77.18; H, 8.97; N, 13.85. Found: C, 77.17; H, 8.98; N, 13.85%.

#### 4.2.5. N-2,3,5,6-tetrametylbenzylimidazoline [L5]

<sup>1</sup>H NMR ( $\delta$ , 300 MHz, CDCl<sub>3</sub>): 2.24, 2.26 (s, 12H, NCH<sub>2</sub>C<sub>6</sub>H(CH<sub>3</sub>)<sub>4</sub>-2,3,5,6), 4.28 (s, 2H, NCH<sub>2</sub>C<sub>6</sub>H(CH<sub>3</sub>)<sub>4</sub>-2,3,5,6), 3.27 and 3.82 (t, *J* = 10.0 Hz, 4H, NCH<sub>2</sub>CH<sub>2</sub>N), 6.69 (s, 1H, NCH<sub>2</sub>C<sub>6</sub>H(CH<sub>3</sub>)<sub>4</sub>-2,3,5,6), 6.98 (s, 1H, NCHN). <sup>13</sup>C NMR ( $\delta$ , 75 MHz, CDCl<sub>3</sub>): 15.5, 20.5 (NCH<sub>2</sub>C<sub>6</sub>H(CH<sub>3</sub>)<sub>4</sub>-2,3,5,6), 54.5 (NCH<sub>2</sub>C<sub>6</sub>H(CH<sub>3</sub>)<sub>4</sub>-2,3,5,6), 46.3, 49.2 (NCH<sub>2</sub>CH<sub>2</sub>N), 131.6, 132.0, 133.4, 134.1, (NCH<sub>2</sub>C<sub>6</sub>H(CH<sub>3</sub>)<sub>4</sub>-2,3,5,6), 156.4 (NCHN). Anal. Calc. for C<sub>13</sub>H<sub>18</sub>N<sub>2</sub> (216.16): C, 77.73; H, 9.32; N, 12.95. Found: C, 77.71; H, 9.33; N, 12.96%.

#### 4.3. Synthesis of W(CO)<sub>4</sub>L<sub>2</sub> (1–5)

All molecules were prepared by similar methods.  $W(CO)_6$  (10 mmol) and *n*-alkylimidazoline ligand (10.1 mmol) were mixed with toluene (20 mL) in empty Schlenk tube which was heated and evacuated with vacuum before use. Solution was refluxed for 1 day under argon and the crude product was precipitated after evaporation of solvent. The yellow product was crystalized with dichloromethane/hexane and dried under vacuum.

#### 4.3.1. (Bis-(N-4-chlorobenzylimidazoline)tetracarbonyltungsten [1]

<sup>1</sup>H NMR ( $\delta$ , 300 MHz, DMSO-*d*<sub>6</sub>): 3.22 and 3.72 (t, 4H, *J* = 10.2 Hz, NCH<sub>2</sub>CH<sub>2</sub>N), 4.47 (s, 2H, NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Cl-4), 7.32 and 7.43 (d, *J* = 8.4 Hz, 4H, NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Cl-4), 7.65 (s, 1H, NCHN). <sup>13</sup>C NMR ( $\delta$ , 75 MHz, DMSO-*d*<sub>6</sub>): 48.1 and 49.5 (NCH<sub>2</sub>CH<sub>2</sub>N), 60.1 (NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Cl-4), 129.1, 130.3, 132.7, 136.1 (NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Cl-4), 163.3 (NCHN), 192.1, 198.4, 204.8 (CO). Anal. Calc. for C<sub>24</sub>H<sub>22</sub>N<sub>4</sub>O<sub>4</sub>Cl<sub>2</sub>W (685.20): C, 42.07; H, 3.24; N, 8.18. Found: C, 42.11; H, 3.28; N, 8.22%. IR (cm<sup>-1</sup>, ATR): 1604 (m, C-N), 1791, 1889, 1997(s, CO).

#### 4.3.2. (Bis-(N-4-metylbenzylimidazoline)tetracarbonyltungsten [2]

<sup>1</sup>H NMR ( $\delta$ , 300 MHz, DMSO- $d_6$ ): 3.12 (t, 2H, J = 5.1 Hz, NCH<sub>2</sub>CH<sub>2</sub>N), 3.62 (t, 2H, J = 5.1 Hz, NCH<sub>2</sub>CH<sub>2</sub>N), 4.34 (s, 2H, NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>-4), 7.07–7.10 (m, 4H, NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub> CH<sub>3</sub>-4), 2.20 (s, 4H, NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>-4), 7.55 (s, 1H, NCHN). <sup>13</sup>C NMR ( $\delta$ , 75 MHz, DMSO- $d_6$ ): 47.9 and 50.0 (NCH<sub>2</sub>CH<sub>2</sub>N), 60.0 (NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>-4), 128.4, 129.6, 133.8, 137.3 (NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>-4), 21.1 (s, 4H, NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>-4), 163.2 (NCHN), 204.8, 214.1 (CO). Anal. Calc. for C<sub>26</sub>H<sub>28</sub>N<sub>4</sub>O<sub>4</sub>W (644.36): C, 48.46; H, 4.38; N, 8.69. Found: C, 48.07; H, 4.50; N, 8.35%. IR (cm<sup>-1</sup>, ATR): 1604 (m, C-N), 1791, 1890, 1995 (s, CO).

## 4.3.3. (Bis-(N-3,5-dimetylbenzylimidazoline)tetracarbonyltungsten [3]

<sup>1</sup>H NMR (300 MHz, DMSO-D<sub>6</sub>)  $\delta$  (ppm) = 2.23 (s, 6H, 3,5-CH<sub>2</sub>C<sub>6</sub>H<sub>3</sub>(CH<sub>3</sub>)<sub>2</sub>), 4.39 (s, 2H, 3,5-CH<sub>2</sub>C<sub>6</sub>H<sub>3</sub>(CH<sub>3</sub>)<sub>3</sub>), 6.88 (s, 2H, 3,5-CH<sub>2</sub>C<sub>6</sub>H<sub>3</sub>(CH<sub>3</sub>)<sub>3</sub>), 6.93 (s, 1H, 3,5-CH<sub>2</sub>C<sub>6</sub>H<sub>3</sub>(CH<sub>3</sub>)<sub>3</sub>), 3.22 and 3.72 (t, J = 9.9 Hz, 4H, NCH<sub>2</sub>CH<sub>2</sub>N), 7.64 (s, 1H, NCHN). <sup>13</sup>C NMR (500 MHz, DMSO-D<sub>6</sub>)  $\delta$  (ppm) = 21.3 (3,5-CH<sub>2</sub>C<sub>6</sub>H<sub>3</sub>(CH<sub>3</sub>)<sub>2</sub>), 48.0 and 50.3 (NCH<sub>2</sub>CH<sub>2</sub>N), 59.9 (3,5-CH<sub>2</sub>C<sub>6</sub>H<sub>3</sub>(CH<sub>3</sub>)<sub>2</sub>), 126.0, 129.5136.0, 138.2 (3,5-CH<sub>2</sub>C<sub>6</sub>H<sub>3</sub>(CH<sub>3</sub>)<sub>2</sub>), 163.4 (NCHN), 204.9, 214.3 (CO). Anal. Calc. for C<sub>28</sub>H<sub>34</sub>N<sub>4</sub>O<sub>4</sub>W (672.42): C, 50.01; H, 4.80; N, 8.33%. Found: C, 50.10; H, 4.72; N, 8.25.%. IR (cm<sup>-1</sup>, ATR): 1609 (m, C-N), 1794, 1855, 1950 (s, CO).



Fig. 4. Diagram of electronic levels of 2 corresponding to gas phase, hexane, and acetonitrile.

#### 4.3.4. (Bis-(N-2,4,6-trimetylbenzylimidazoline) *tetracarbonyltungsten* [4]

<sup>1</sup>H NMR (300 MHz, DMSO-D<sub>6</sub>)  $\delta$  (ppm) = 2.30 and 2.32 (s, 9H, 2,4,6-CH<sub>2</sub>C<sub>6</sub>H<sub>2</sub>(CH<sub>3</sub>)<sub>3</sub>), 4.29 (s, 2H, 2,4,6-CH<sub>2</sub>C<sub>6</sub>H<sub>2</sub>(CH<sub>3</sub>)<sub>3</sub>), 6.91 (s, 2H, 2,4,6-CH<sub>2</sub>C<sub>6</sub>H<sub>2</sub>(CH<sub>3</sub>)<sub>3</sub>), 3.28 and 3.78 (t, J = 5.4 Hz, 4H, NCH<sub>2</sub>CH<sub>2</sub>N), 6.91 (s, 1H, NCHN). <sup>13</sup>C NMR (500 MHz, DMSO-D<sub>6</sub>)  $\delta$  (ppm) = 19.8 and 21.0 (2,4,6-CH<sub>2</sub>C<sub>6</sub>H<sub>2</sub>(CH<sub>3</sub>)<sub>3</sub>), 45.1 and 48.9 (NCH<sub>2</sub>CH<sub>2</sub>N), 59.6 (2,4,6-CH<sub>2</sub>C<sub>6</sub>H<sub>2</sub>(CH<sub>3</sub>)<sub>3</sub>), 129.6, 129.7, 127.8, 137.2 (2,4,6-CH<sub>2</sub>C<sub>6</sub>H<sub>2</sub>(CH<sub>3</sub>)<sub>3</sub>), 161.0 (NCHN), 191.2, 204.1, 213.7 (CO). Anal. Calc. for C<sub>30</sub>H<sub>36</sub>N<sub>4</sub>O<sub>4</sub>W (700.47): C, 51.44; H, 5.18; N, 8.00. Found: C, 51.38; H, 5.15; N, 8.07%. IR (cm<sup>-1</sup>, ATR): 1598 (m, C-N), 1787, 1837, 1990 (s, CO).

#### 4.3.5. (Bis-(N-2,3,5,6-tetrametylbenzylimidazoline) tetracarbonyltungsten [5]

<sup>1</sup>H NMR ( $\delta$ , 300 MHz, DMSO- $d_6$ ): 3.19 (t, 2H, l = 10.5 Hz, NCH<sub>2</sub>CH<sub>2</sub>N), 3.63 (t, 2H, J = 10.5 Hz, NCH<sub>2</sub>CH<sub>2</sub>N), 4.51 (s, 2H, NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>)<sub>4</sub>), 6.97 (s, 1H, NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>)<sub>4</sub>), 2.16 (s, 6H, NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>)<sub>4</sub>), 2.18 (s, 6H, NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>)<sub>4</sub>), 7.34 (s, 1H, NCHN). <sup>13</sup>C NMR (δ, 75 MHz, DMSO-*d*<sub>6</sub>): 45.1 and 48.2 (NCH<sub>2</sub>CH<sub>2</sub>N), 59.7 (NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>)<sub>4</sub>), 131.8, 133.6134.0 (NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>)<sub>4</sub>), 20.6 (NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>)<sub>4</sub>), 15.7 (NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>)<sub>4</sub>), 162.5 (NCHN), 204.8 (CO). Anal. Calc. for C<sub>32</sub>H<sub>40</sub>N<sub>4</sub>O<sub>4</sub>W (728.52): C, 52.76; H, 5.53; N, 7.69. Found: C, 52.80; H, 5.60; N, 7.65%. IR (cm<sup>-1</sup>, ATR): 1596 (m, C-N), 1785, 1810, 1988 (s, CO).

#### 4.4. Calculation method

DFT/TDDFT calculations for full unconstrained geometry optimizations and electronic transitions were carried out with ORCA [24] version 2.8 using the exchange functional according to Becke [15] and the correlation functional suggested by Perdew [16,17], hereafter called BP, with the resolution-of-the-identity (RI) approximation, a TZV [18] basis set, the tightscf and grid4 options. The COSMO solvation model was used for analyzing the solvent effects on all calculations. Scalar relativistic effects were treated using the Zeroth Order Regular Approximation (ZORA) formalism [19–21]. To speed up the calculations TZV/J auxiliary basis set was used [23].

#### 4.5. X-ray crystallography

Suitable crystals of 4 and 5 were selected for data collection which were performed on Bruker X8-Apex II (for 4) and STOE IPDS II (for 5) diffractometer equipped with a graphite-monochromatic Mo-K<sub> $\alpha$ </sub> radiation at 296 K. The structures were solved by direct methods using SHELXS-97 [56] and refined by full-matrix leastsquares methods on  $F^2$  using SHELXL-97 [56] from within the WINGX [57] suite of software. All non-hydrogen atoms were refined with anisotropic parameters. The H atoms were located from different maps and then treated as riding atoms with C-H distances of 0.93–0.97 Å. Molecular diagrams were created using MERCURY [58]. Details of data collection and crystal structure determinations are given in Table 1. The molecular structure of molecules with the atom labeling is shown in Fig. 2.

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#### Appendix A. Supplementary data

Supplementary data related to this article can be found at http:// dx.doi.org/10.1016/j.molstruc.2016.07.002.

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