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### The Study of Substituent effect on Osmabenzene complexes

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#### Abstract:

The electronic structure and properties of the osmaabenzenes and *para* substituted osmabenzenes have been explored using the hybrid density functional mpw1pw91 theory. Systematic studies on the substituent effect in *para* substituted osmabenzenes complexes have been studied. The following substituents were taken into consideration: H, F, CH<sub>3</sub>, OH, NH<sub>2</sub>, CN, NO<sub>2</sub>, CHO, and COOH. Basic measures of aromatic character were derived from the structure and nucleus-independent chemical shift (NICS). The NICS calculations indicate a correlation between NICS(1.5) and the hardness in all species. Quantum theory of atoms in molecule analysis (QTAIM) indicates a correlation between  $\rho$ (Os-C) bonds and the electron density of bond critical point in all species.

**Keywords:** Osmabenzene, substituent effect, DFT calculations, (QTAIM), (NICS)

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## 1. Introduction

Metallabenzenes are six-membered metallacycles analogous to benzene for which one CH unit has been replaced by an isolobal transition-metal fragment  $\{ML_n\}$  (1-3). For the past decade the synthesis of metallabenzenes have has studied (4). The first metallabenzene to be isolated and characterized was osmabenzene  $Os(C_5H_4[S])(CO)(PPh_3)_2$ , the  $OsC_5$  ring was assembled from two ethyne molecules and a single carbon atom from the thiocarbonyl ligand already resident on the osmium in the starting material,  $Os(CS)(CO)(PPh_3)_{3(5-6)}$ . The structure and properties of osmabenzenes have been studied experimentally and theoretically(7-12). From experimental and theoretical examinations one sees that the actual experimental knowledge concerning osmabenzenes compounds is still relatively limited due to the subtle nature of such compounds. In the present study, the geometries, aromaticity and chemical bonding of osmabenzenes and *para* substituted osmaabenzenes are studied theoretically. The analysis of the electron density within the AIM methodology has been used for providing valuable information on characterizing the molecules based on their critical points.

## 2. Computational Methods

All calculations were carried out with the Gaussian 2003 suite of program(13) using the standard 6-31G(d,p) basis set calculations of systems contain C, H, N, F and O (14-15). For Os element standard LANL2DZ basis set(16-18) are used and Os described by effective core potential (ECP) of Wadt and Hay pseudopotential(19) with a doublet- $\xi$  valance using the LANL2DZ. Geometry optimization was performed utilizing One Parameter Hybrid Functional with Modified Perdew-Wang Exchange and Correlatio (mpw1pw91)(20). A vibrational analysis was performed at each stationary point found, that confirm its identity as an energy minimum.

The nucleus independent chemical shift (NICS) was used as a descriptor of aromaticity from the magnetic point of view. The index is defined as the negative value of the absolute magnetic shielding computed at ring centers(21) or another interesting point of the system(22). Rings with highly negative values of NICS are quantified as aromatic by definition, whereas those with positive values are anti-aromatic.

The AIM2000 program was used for topological analysis of electron density(23). The following characteristics of ring critical points (RCPs) are taken into account: density at RCP ( $\rho(rc)$ ), its Laplacian ( $\nabla^2(r_c)$ ).

### 3. Result and discussion

#### 3.1 Bond distances

As it can be seen in Table 1, the Os–C bonds length in substituted  $C_5H_4XOs(PH_3)_2(CO)Cl$  is changing due to the presence of the substituent in *para* position of the osmabenzene ring (Figure 1). For the strongest electron donating substituents the Os–Cl bond is longer than in for the electron donating substituents. Therefore, the electron withdrawing substituents additionally stabilize the Os–C bond, while the electron donating ones weaken it. In addition to that, the Os–Cl bonds are relatively longer than their Os–C5 counterparts. This can be explained by the presence of the chlorine ligand, which, as a lower field ligand than the CO one, weakens the *cis*-placed Os–CO bonds.

On the other hand, the Os–C(O) bonds are shorter in donating electron. The increasing of metal charge in the presence of is electron donating substituents causes to increasing back bonding in Os–C(O) bond, while the electron donating ones increase it.

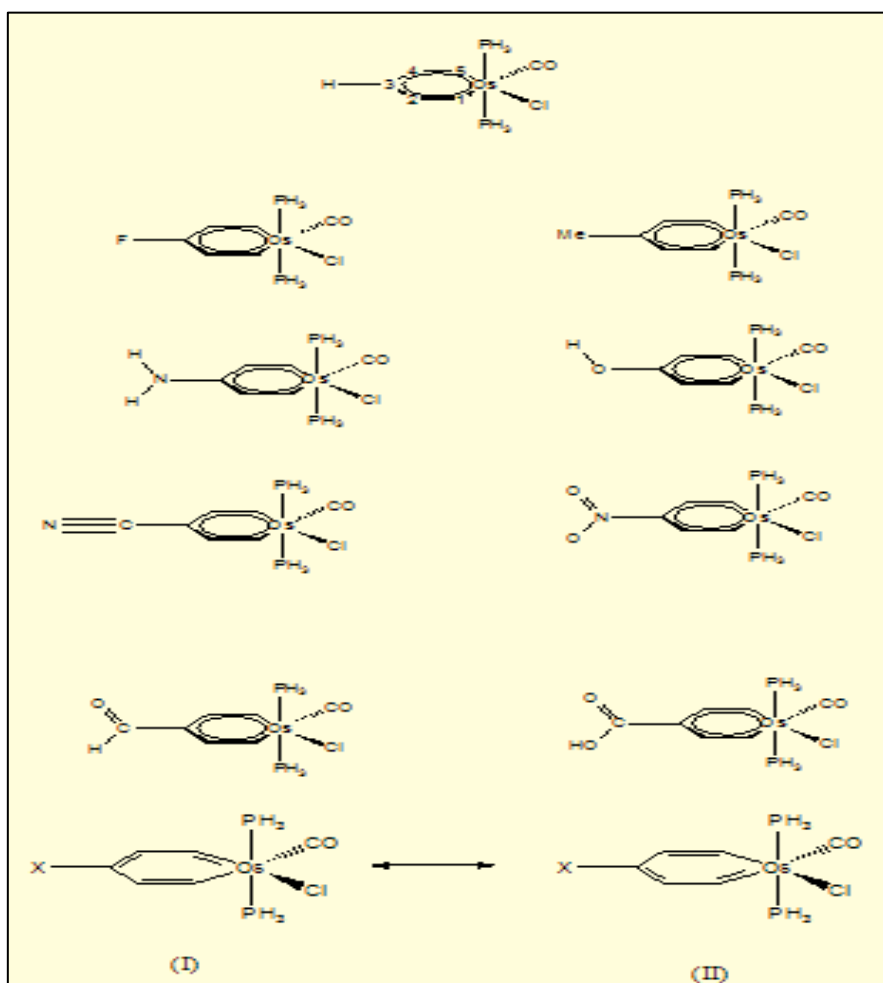


Figure 1. *para*-Substituted  $C_5H_4XOs(PH_3)_2(CO)Cl$  complexes.

### 3.2 Frontier orbital energies and chemical hardness.

The frontier orbital energies and the hardness of all complexes computed are given in the Table 2. These values indicate the energy of the frontier orbitals are lower in the case of electron-withdrawing substituents. There is even a direct relation between the frontier orbital energy with  $r(\text{Os-C(O)})$  and the bonds length average of ring (Figure 2).

To evaluate the hardness and chemical potential of these complexes, these values can be calculated from the HOMO and LUMO orbital energies using the following approximate expression:

$$\mu = (\epsilon_{\text{HOMO}} + \epsilon_{\text{LUMO}})/2$$

$$\eta = (\epsilon_{\text{HOMO}} - \epsilon_{\text{LUMO}})/2$$

Where  $\mu$  is the chemical potential (the negative of the electronegativity), and  $\eta$  is the hardness (24-25).

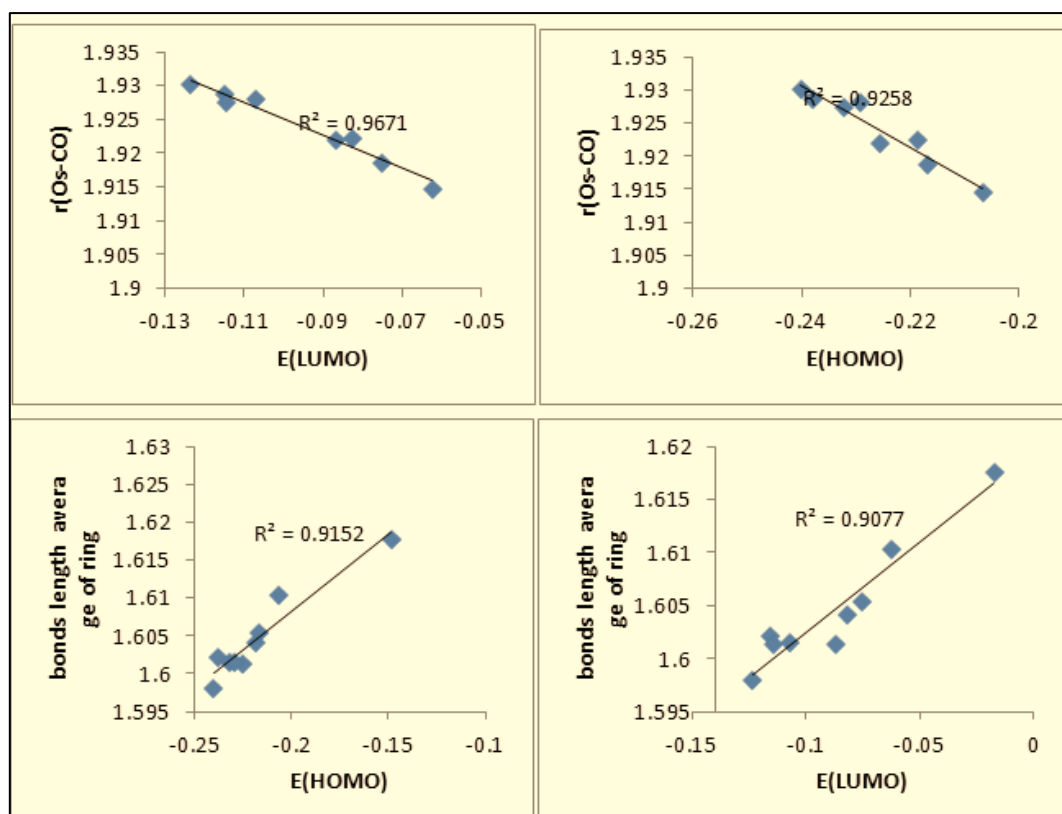


Figure 2. A linear correlation between frontier orbital energy values with Os-C(O) bond length and bonds length average of ring in substituted complexes.

The hardness values of in Table 2 indicate the increasing of these values in donating substituents. On the other hand, these values decrease in electron-withdrawing substituents.

The collected values of chemical potential in Table 3 show that the increasing of these values in donating substituents. From the other point of view, these values decrease in electron-withdrawing substituents. Also, the electrophilicity values of electron-withdrawing substituents are more than electron-donating substituents.

Table 1. Bond distances values for *para*-substituted  $C_5H_4XOs(PH_3)_2(CO)Cl$  complexes.

X	Os-C1	C1-C2	C2-C3	C3-C4	C4-C5	C5-Os	Os-P	Os-C(O)
H	2.09250	1.37971	1.43072	1.39170	1.42151	1.99031	2.36857	1.93913
F	2.07529	1.36724	1.41022	1.38290	1.39683	1.97576	2.34132	1.92213
Me	2.07430	1.36640	1.42351	1.38964	1.40164	1.96947	2.33919	1.92234
OH	2.08020	1.36338	1.42048	1.39803	1.38949	1.98151	2.33781	1.91879
NH2	2.08422	1.35905	1.43295	1.41113	1.38119	1.99360	2.33320	1.91475
CN	2.06595	1.36873	1.42237	1.38968	1.40550	1.96152	2.34747	1.92867
NO <sub>2</sub>	2.06461	1.37099	1.40900	1.37636	1.40906	1.95861	2.34799	1.93019
COOH	2.06757	1.37013	1.41857	1.38489	1.40621	1.96159	2.34403	1.92771
CHO	2.06723	1.37034	1.41645	1.38536	1.40476	1.96525	2.34494	1.92813

Table 2. Frontier orbital energies (Hartree), HOMO-LUMO gap energy (eV), hardness (eV), chemical potential (eV), and electrophilicity ( $\omega$ ) for *para*-substituted  $C_5H_4XOs(CO)(PH_3)_2Cl$  complexes.

	HOMO	LUMO	Gap	$\eta$	$\mu$	$\omega$
H	-0.14846	-0.01750	3.563631	1.781816	-2.25802	1.430745
F	-0.22563	-0.08675	3.779147	1.889574	-4.25018	4.779922
Me	-0.21862	-0.08245	3.705404	1.852702	-4.0963	4.52843
OH	-0.21719	-0.07545	3.856972	1.928486	-3.9816	4.110258
NH2	-0.20677	-0.06237	3.929355	1.964678	-3.66187	3.412584
CN	-0.23807	-0.11535	3.339408	1.669704	-4.80856	6.924063
NO <sub>2</sub>	-0.24032	-0.12348	3.179403	1.589702	-4.94979	7.705981
COOH	-0.22936	-0.10695	3.330972	1.665486	-4.57577	6.285745
CHO	-0.23239	-0.11444	3.209608	1.604804	-4.7189	6.937923

### 3.3 Nucleus-independent chemical shift analysis (NICS)

The nucleus-independent chemical shift (NICS) method has been widely employed to characterize the aromaticity(26). As an effort to discuss the use of NICS as a measure of aromaticity for six-membered, we have calculated NICS values along the z-axis to the ring plane beginning on the center of the ring up to 2.0 Å. These calculations show that the shape of NICS profile with respect to the distance from the ring center is similar. In addition, for all species, we have localized the NICS maxima and minima and determined the distances to the center of the ring at which they occur. See Table 3. For all molecules, the highest absolute value of NICS is 1.5 Å above the center of the ring. It is possible that induced magnetic fields generated by the  $\pi$  aromaticity indicate a minimum NICS at the certain distance from the center of the ring. From Table 3,

it can be seen that all six-membered ring compounds have large negative NICS values, indicating their enhanced aromatic properties. All these NICS values are mainly attribute to the delocalized  $\pi$  electrons

current. Theoretical computation of all molecules shows that there was a linear correlation between NICS(1.5) values and hardness (Figure 3). These values show that aromaticity increases in electron-withdrawing substituents.

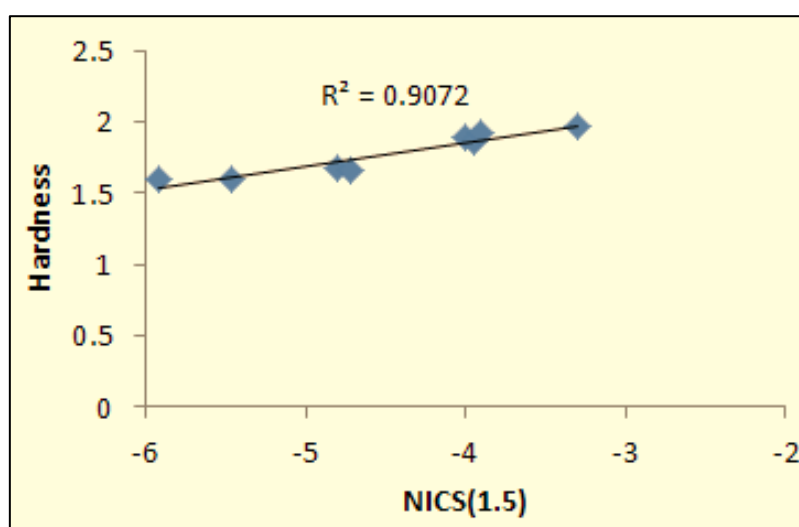


Figure 3. A linear correlation between NICS(1.5) values and hardness of complexes

Table 3. the NICS(0.0), NICS(0.5), NICS(1.0), NICS(1.5), and NICS(2.0) (ppm) values for *para*-substituted  $C_5H_4XOs(PH_3)_2(CO)Cl$  complexes.

X	NICS(0.0)	NICS(0.5)	NICS(1.0)	NICS(1.5)	NICS(2.0)
H	1.5071	-0.7367	-3.3980	-3.7066	-3.0810
F	-0.4657	-2.3052	-4.2026	-4.0044	-3.0656
Me	0.9065	-1.2708	-3.7602	-3.9446	-3.1539
OH	-1.0476	-2.6709	-4.2491	-3.9026	-3.0000
NH <sub>2</sub>	-0.5886	-2.0525	-3.5029	-3.3026	-2.6339
CN	-0.3399	-2.5924	-4.9658	-4.7971	-3.6710
NO <sub>2</sub>	-2.3546	-4.6976	-6.7633	-5.9232	-4.3155
COOH	0.4867	-1.9831	-4.7104	-4.7223	-3.6474
CHO	-0.7485	-3.3045	-5.8783	-5.4652	-4.0799

#### 4. QTAIM analysis

It has been proved, that the AIM-based analysis of electron density can provide valuable information on many physical and chemical properties of the molecular systems (27-31). (It is fair to mention here some criticism of AIM Quantum Theory. For this criticism see Ref.(32-34)) It has been found for instance that the

value of electron density ( $\rho$ ) and its laplacian ( $\nabla^2\rho$ ) estimated at bond critical point (BCP) of a given bond correlate very well with the strength of this bond, as well as with its length, since, as it is well known, both the strength and the length of a given bond are mutually dependent (35-39). Also in this case such a relationship can be observed and the linear regression can be found between  $\rho(\text{Os-C})$  and  $r(\text{Os-C})$  in all complexes (Figure 4).

Table 4. Electron densities  $\rho$  ( $e/a_0^3$ ), Laplacians  $\nabla^2\rho$  ( $e/a_0^5$ ), total electron energy density,  $H(\rho)$ , kinetic energy density,  $G(\rho)$ , and potential energy density,  $V(\rho)$  at (a)the ring center, (b)Os-C critical, and (c)Os-CO points for *para*-substituted  $\text{C}_5\text{H}_4\text{XOs}(\text{PH}_3)_2(\text{CO})\text{Cl}$  complexes.

(a)ring center		
X	$\rho(3,+1)$	$\nabla^2\rho(3,+1)$
H	0.01478	0.08973
F	0.01537	0.09541
Me	0.01550	0.09668
OH	0.01527	0.09494
NH <sub>2</sub>	0.01512	0.09384
CN	0.01546	0.09571
NO <sub>2</sub>	0.01583	0.09703
CHO	0.01564	0.09565
COOH	0.01566	0.09670

(b)Os-C1					
X	$\rho$	$\nabla^2\rho$	G	H	V
H	0.12011	0.25344	0.11110	-0.04774	-0.15884
F	0.12364	0.27168	0.11808	-0.05016	-0.16824
Me	0.12451	0.26181	0.11663	-0.05118	-0.16781
OH	0.12239	0.26816	0.11630	-0.04926	-0.16555
NH <sub>2</sub>	0.12096	0.26826	0.11518	-0.04811	-0.16330
CN	0.12662	0.26759	0.11962	-0.05272	-0.17233
NO <sub>2</sub>	0.12726	0.26784	0.12020	-0.05324	-0.17345
COOH	0.12666	0.26243	0.11853	-0.05292	-0.17146
CHO	0.12655	0.26448	0.11890	-0.05278	-0.17167

(b)Os-C5					
X	$\rho$	$\nabla^2\rho$	G	H	V
H	0.14841	0.27619	0.13949	-0.07044	-0.20992
F	0.15284	0.27727	0.14370	-0.07438	-0.21808
Me	0.15543	0.26900	0.14427	-0.07702	-0.22129
OH	0.15069	0.27712	0.14167	-0.07239	-0.21406
NH <sub>2</sub>	0.14720	0.26954	0.13676	-0.06938	-0.20614
CN	0.15790	0.27194	0.14728	-0.07929	-0.22657
NO <sub>2</sub>	0.15911	0.27264	0.14861	-0.08045	-0.22907
COOH	0.15848	0.26345	0.14593	-0.08007	-0.22599
CHO	0.15734	0.26326	0.14480	-0.07899	-0.22379

(c)Os-C(O)					
X	$\rho$	$\nabla^2\rho$	G	H	V
H	0.14056	0.55242	0.19575	-0.05764	-0.25339
F	0.14624	0.56504	0.20372	-0.06246	-0.26619
Me	0.14623	0.56315	0.20345	-0.06266	-0.26611
OH	0.14708	0.56920	0.20541	-0.06311	-0.26853
NH <sub>2</sub>	0.14821	0.57503	0.20769	-0.06393	-0.27162
CN	0.14450	0.55567	0.20019	-0.06128	-0.26147
NO <sub>2</sub>	0.14418	0.55332	0.19942	-0.06109	-0.26051
COOH	0.14492	0.55591	0.20071	-0.06173	-0.26244
CHO	0.14474	0.55554	0.20041	-0.06153	-0.26195

Additional valuable information on chemical bond properties is available from the total electron energy density,  $H(\rho)$ , and its components; kinetic electron energy density,  $G(\rho)$ , positive by definition, and potential electron energy density,  $V(\rho)$ , negative by definition. The following relation is known for  $H(\rho)$  and its components (40-41):

$$H(\rho) = V(\rho) + G(\rho)$$

It is known that in the region of the bond CP of weak closed-shell interatomic interactions the kinetic energy density dominates, with  $G(\rho)$  magnitude being slightly greater than the potential energy density  $|V(\rho)|$  which implies the total energy density  $H(\rho) > 0$  and close to zero, whereas for strong covalent interactions  $V(\rho)$  dominates over the kinetic energy density and  $H(\rho) < 0$ . This is usually accompanied by  $\nabla^2\rho > 0$  for the proper case and  $\nabla^2\rho < 0$  for the latter one (there is one exception mentioned in the further part of the discussion).

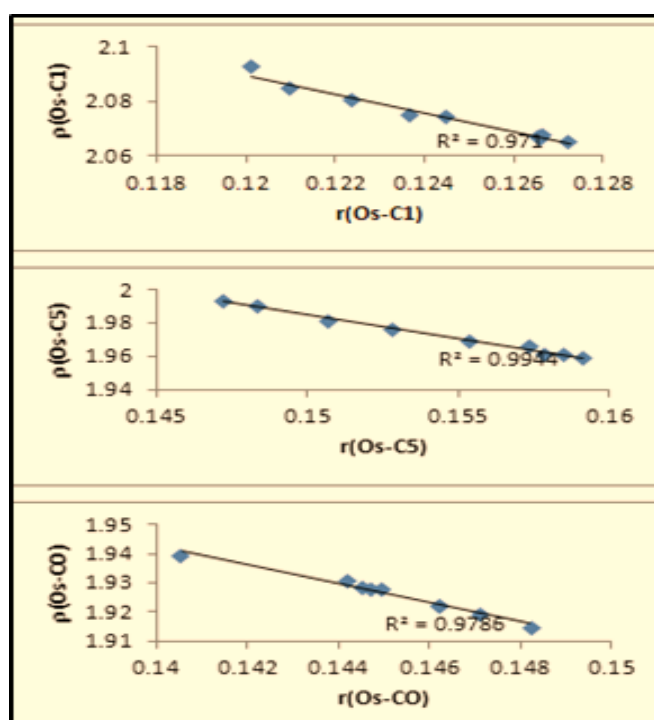


Figure4. A linear correlation between  $r(\text{Ru-C})$  values and  $\rho(\text{Ru-C})$  of complexes.



#### 4.1 Os–C bond

Interestingly, both  $G(\rho)$  and  $|V(\rho)|$  values increase with electron-withdrawing properties of substituents in the *para*-position of the osmabenzene ring. However,  $H(\rho)$  is invariably positive and very close to zero. Probably, this could be due to the changes in the Os–C bond length. As already mentioned, the Os–C distances decrease with an increase of electron-withdrawing properties of the attached substituents. It can thus be expected that the shorter is the bond, the more covalent is its character, which implies an increase of  $|V(q)|$  magnitude.

However, this is compensated by an increase of  $G(q)$  which is related with Pauli repulsion between two closed shells. As a result, the  $H(q)$  varies within a very small range. These changes are relatively small because of a limited possibility of the influence of substituents on the Os–C bond, and can be more significant in the case of a larger spectrum of variability of a given bond.

#### 4.2 Os–C(O) bond

It is worth mentioning here that the introduction of a given substituent into position 4 of the osmabenzene ring results in small but systematic changes in the Os–C(carbonyl) bonding.

These values indicated, in the case of all Os–C<sub>carbonyl</sub> bonds  $\nabla^2\rho$  values at corresponding BCPs are positive, as it was found for closed-shell interactions.

On the other hand, the  $H(\rho)$  values are negative, as found for shared interactions. This is in agreement with observations made for the Ti–C bonds in titanium complexes (41), in the case when the metal–ligand bonding has a characteristic that represents a mix of the closed-shell and shared parameters.

Moreover, the  $H(\rho)$  values are more negative for Os–C5 bonds, which is directly connected with relative greater predominance of  $|V(q)|$  magnitude over the  $G(q)$  magnitude. This suggests a more covalent character of the Os–C5 bond as compared with the Os–C1, and is also in line with general knowledge, according to which low-field ligands (e.g. chlorine) weaken the *cis* placed M–C bonds. Generally, the greater value of  $|H(\rho)|$  (with negative sign), the more covalent character of the bond. It seems therefore that the covalent character of the Os–C(O) bonds increases with electron donating properties of the substituent attached to the osmabenzene.

This can be partially connected with the trans-effect and the fact that a relatively greater contribution of structure (I) in Fig. 1 should lead to an increase of back-donation in the *trans* placed Os–C<sub>carbonyl</sub> bond. As a result, it can be said that in the analyzed organometallic species the Os–C(carbonyl) bonding has a more covalent character than the Os–C(osmabenzene) bonding.

## 5. Conclusion

The theoretical study of structure and properties in the osmabenzene and substituted osmabenzene complexes is indicated:

1. The Os-C bond distances show that systematic variations in *para* substituted osmaabenzene complexes
2. Analysis of frontier orbitals shows the decreasing of the hardness and E(LUMO) in electron-withdrawing substituents.
3. There is the delocalized  $\pi$  electrons current in the basis of the NICS(1.5) values. Also, aromaticity increases in electron-withdrawing substituents.
4. The QTAIM analysis indicates the covalent character of the Os-C5 bond is more than Os-C1. Also, this property of Os-C(O) bonds increases with electron donating properties of the substituent.

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