Introduction

Ever since Hoffmann et al.1 brought the concept of planar tetracoordinate carbon (pC) to the world’s attention, stabilization of a pC has been viewed as a fascinating challenge given to chemists. Hoffmann and co-workers proposed that stabilization of pC can be achieved either through a mechanical approach by constraining the geometry in such a way that the central carbon and its neighbours are in one plane or through an electronic approach by incorporating suitable substituents (ions, metal centers) where at least one of the coordinations should be an atom other than carbon.1–3 Schleyer and co-workers proposed that stabilization of pC can also be possible by incorporating the carbon into small ring systems.4–6 Another widely used approach for the stabilization of pC centers is through the introduction of transition metals. A divanadium complex of formula V₂[(OMe)₂C₆H₃]₂ was the first crystallographically characterized molecule to show a pC center.7 Later many bimetallic complexes containing pC centers have been reported with different metal centers like Ti, Pd, W, Re and Ce.8–13 Along with bimetallic systems, some mononetallic complexes are known to possess pC centers where the planar tetracoordination results from the additional interaction of the carbon with the metal center.14 It was observed that in some zirconocene complexes the fourth bond of the carbon is the result of the CH agostic interaction with the metal center.15,16 Similar unusual bonding interactions were reported in the case of metallacyclobutadienes, metallacyclopentadienes, and other small metalacycles.17–20 Many reviews dealing with the progress in the field of planar tetra- and hypercoordinate carbon systems are available in the literature.12,21–25

Recently, the metallacyclobutadiene (MCBD) intermediate of alkynemetathesis has been proposed as a pC complex wherein the pC center is the β-carbon of the MCBD,26,27 MCBD intermediates of alkynemetathesis, especially with tungsten catalysts, are stable, and many crystal structures28–30 are available in the Cambridge Structural Database (CSD) and theoretical studies have also established them as minimum energy structures.31,32 Structurally, the pC nature of the MCBD is assigned on the basis of short single-bond like MC distances (2.20–2.40 Å). Based on energy decomposition, bond order and electron density analyses, significant bonding interaction between metal and the β-carbon has been unambiguously proven in the case of a Schrock tungsten complex Cl₂W(C=MeC=Me=C=Bu) (CSD ID BONXOR) (Fig. 1a). This bond named as the 1,3-MC bond provided the fourth coordination for the carbon along with three other bonds (two CC and one CH bonds) in the plane of the metallacycle (Fig. 1a).26

Three decades ago, Schrock et al. reported the unexpected formation of ‘deprotio’ metallocycles during the course of
metathesis reactions of terminal alkynes with molybdenum and tungsten catalysts. For instance, the reaction of WCp(C₆H₄Bu)Cl₂ with C₆H₄BuCH in triethyl amine yielded the metallacycle WCpCl[C₆H₄Bu-CH₃] (CSD ID CEGGAW, Fig. 1a) instead of the expected MCBD WCpCl₂[C₆H₄Bu-CH₃] due to dehydrohalogenation. A short WC distance of 2.049 Å in WCpCl[C₆H₄Bu-CH₃] indicated bond formation. Recently, Jemmis et al. have studied structurally similar group 4 ‘deproti’ metallacycles known as metallacycloallenes using molecular orbital and natural bond orbital analyses and confirmed that four-membered metallacycloallenes are stabilized through metal-C₆ bond interaction. Although the C₆ of metallacycloallene or a ‘deproti’ metallacycle is not a ptC center (only 3 atoms, viz. two C₆ are metal center bonded to C₆), WCpCl[C₆-tBuCC₆-tBu] has been considered in this study to assess the strength of the 1,3-MC type interaction in the MCBD.

Recently, Suresh and Frenking showed the existence of the 1,3-MC bond in the MCBD systems of group 4, 5 and 6 transition metals. This bonding is due to considerable dₓ⁻Pₓ interaction between the metal and C₆ and this finding paves the way for a new type of ptC chemistry in organometallics. Compared to the previous theoretical and experimental discoveries on ptC centers, the finding that a ptC center is available in MCBD is more fascinating because of the role it plays in the alkyn metathesis reaction as well as the status of the complex as a well-defined, stable, structurally characterized organometallic complex. The MCBD system can also be viewed as a system wherein the metal center is incorporated into a small carbon framework. Such a metallic incorporation into carbon frameworks can drastically change the properties of the resulting molecules and, on the basis of it, new materials exhibiting interesting optical, electronic and magnetic properties can be designed and developed. Thus, the stable form of ptC in MCBD offers new design strategies for the development of ptC based materials. Using the extension of the building block in Fig. 1b, Suresh and Frenking have computationally designed “edge complexes” of group 4 transition metals by utilizing the 1,3-MC bonding at the edges of aromatic hydrocarbons. Herein, we propose that the structural motif given in Fig. 1b for a ptC center can be extended to design more complex architectures in 1, 2 and 3 dimensions. The larger structures can be envisaged by extending the structure in the X-, Y- and Z-directions via the β-carbon, α-carbon and the metal center, respectively (Fig. 1b). Many computational attempts have been made in the past to design the possible extension of molecules possessing multiple ptC centers in complex networks. Prediction of edge decorated graphene systems possessing ptC centers is also proposed by many groups by incorporating metal centers and some non-metals.

In this work, we wish to emphasize that the ptC center, as well as the 1,3-MC bond observed in an MCBD system of alkyn metathesis, is fundamental to organometallic chemistry and these findings immediately open up new room for expanding the chemistry of ptC through 1,3-MC bonds in CC frameworks. We performed this study as a computational endeavour for the design of ptC incorporated metal–organic frameworks.

### Computational details

For the optimization of crystal structures and 1- and 2-dimensional structures, the BP86/BS1 level of density functional theory (DFT) is used wherein BS1 stands for the triple-zeta valence quality basis set def2-tzvpp for all the atoms and the use of effective core potential for W to treat the core electrons. For the optimization of large 3-dimensional cage structures, the BP86/BS2 level is used wherein BS2 stands for the all-electron basis set SDD with effective core potential for W and the 6-31g* basis set for other elements. BP86 is a GGA functional containing the Becke 1988 exchange functional and the Perdew 86 correlation functional. All the calculations have been carried out with the Gaussian09 program. All the structures discussed in this work have been confirmed as energy minima by locating only positive frequency for all the normal modes of vibration unless otherwise specified. Wiberg bond order analysis is performed to quantify bond strength using Natural Bond Orbital (NBO) analysis as implemented in Gaussian09. Electron density topology analysis is performed using the AIMALL program. For 13C-NMR analysis, the GIAO method in Gaussian09 is used. The same method is used to calculate Nucleus Independent Chemical Shift values at the center of the ring, NICS(0), at 1 Å above the ring center, NICS(1), and also the zz-tensor component of NICS(1)z. Aromaticity of the MCBD ring is visualized in terms of Anisotropy of Induced Current Density (AICD) developed by the Herges group.
Results and discussion

At first, we consider X-ray crystal structures of seven tungsten-cyclobutadiene (WCBD) systems (Fig. 2) for the structural and bonding analyses to confirm the existence of the 1,3-MC bond. Among them, the first three systems, identified in the CSD as WEMYIY, WEMYOE, and WEMYUK, were reported in a very recent work by Veige et al.\textsuperscript{59} They have synthesized the first neutral trianionic ONO pincer-type tungsten alkylidyne complexes and showed that these complexes can react rapidly with alkyynes to yield WCBDs. Though the possibility of a 1,3-MC bond in these structures is obvious from the single bond-like $\text{WC}_\beta$ distance ($\sim$2.15 Å), this kind of bonding was not discussed by Veige et al. In Fig. 2, we also depict the schematics of the molecular geometries of WCBD systems reported by Schrock and co-workers and identified in CSD as COMREB,\textsuperscript{17} CONISH\textsuperscript{18} and CUYJEL.\textsuperscript{19} Yet another WCBD system is KISGID reported by Tamm et al.\textsuperscript{30} In Table 1, the bond length ($\text{WC}_\alpha$, $\text{WC}_\beta$ and $\text{C}_\alpha\text{C}_\beta$) and bond angle ($\text{C}_\alpha\text{C}_\beta\text{C}_\alpha$) parameters of the metallacycle region are depicted for the X-ray structures and the corresponding theoretically derived structures.

None of the structures show any kind of symmetry as they possess dissimilar $\text{WC}_\alpha$ and $\text{C}_\alpha\text{C}_\beta$ bond distances. It is gratifying that the computed values of the distance, particularly the $\text{WC}_\beta$ distance and bond angles (Table 1), show good agreement with experimental values. In addition to the $\sigma$-type bonding interaction between W and $\text{C}_\alpha$, the $\pi$-type interactions between metal d-orbitals and the carbon p-orbital give substantial double bond character to the $\text{WC}_\alpha$ bond. As a result, $\text{WC}_\alpha$ bonds show a significantly shorter distance than the typical WC single bond (2.10 Å). The strongest evidence that supports the existence of a 1,3-MC bond in these complexes is the single bond-like $\text{WC}_\beta$ distance. Both theory and experiment agree that the $\text{WC}_\beta$ distance in the range 2.093–2.234 Å is well within the sum of the van der Waals radii of tungsten and carbon ($\sim$3.8 Å) and is comparable with the $\text{WC}_\beta$ distance in the ‘deproti’ metallacycle CEGGAW (2.05 Å). The good agreement between the gas phase optimized $\text{WC}_\beta$ data and the corresponding crystal data clearly suggests that the single bond-like $\text{WC}_\beta$ distance cannot be neglected as a consequence of the structural restriction imposed on the four-membered ring or due to crystal packing.

QTAIM analysis

In the QTAIM parlance, affirmation of the bonding interaction between two atoms is verified by locating a (3,–1) critical point (known as the bond critical point (BCP)) and the associated atomic interaction line (known as the bond path (BP)) between the interacting atoms. The issue of the use of BP as a universal indicator of bonding is highly debated in the litera-

![Fig. 2 Molecular drawing of the crystal structures of tungstenacyclobutadienes. CSD ID is used to name the molecules.](image)

| Table 1 Structural parameters of WCBD in the crystal and in the optimized geometries given in parentheses (bond distances are given in Å and angles in degrees) |
|---------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| MCBD            | $\text{WC}_\alpha$ | $\text{WC}_\alpha$ | $\text{C}_\alpha\text{C}_\beta$ | $\text{C}_\alpha\text{C}_\beta$ | $\text{WC}_\beta$ | $\text{<C}_\alpha\text{C}_\beta\text{C}_\alpha$ |
| WEMYIY         | 1.905            | 1.911            | 1.450            | 1.473            | 2.159            | 119.9           |
| (1.935)         | (1.943)          | (1.452)          | (1.468)          | (2.192)          | (120.5)          |
| WEMYOE         | 1.897            | 1.911            | 1.443            | 1.473            | 2.156            | 119.9           |
| (1.930)         | (1.938)          | (1.450)          | (1.467)          | (2.185)          | (120.5)          |
| WEMYUK         | 1.882            | 1.908            | 1.453            | 1.456            | 2.143            | 120.0           |
| (1.927)         | (1.936)          | (1.459)          | (1.464)          | (2.185)          | (120.3)          |
| COMREB         | 1.883            | 1.949            | 1.433            | 1.466            | 2.159            | 120.8           |
| (1.903)         | (1.986)          | (1.417)          | (1.490)          | (2.193)          | (121.0)          |
| CONISH         | 1.864            | 1.903            | 1.428            | 1.437            | 2.093            | 122.5           |
| (1.926)         | (1.930)          | (1.436)          | (1.481)          | (2.164)          | (121.3)          |
| CUYJEL         | 1.890            | 1.921            | 1.417            | 1.499            | 2.103            | 123.1           |
| (1.939)         | (1.942)          | (1.428)          | (1.466)          | (2.134)          | (124.3)          |
| KISGID         | 1.879            | 1.992            | 1.387            | 1.533            | 2.209            | 119.3           |
| (1.901)         | (2.024)          | (1.397)          | (1.519)          | (2.234)          | (120.0)          |
ture and many people have commented on that the detection of a BP or BCP is not necessary to verify the bonding interaction between two atoms.\textsuperscript{50–67}

In the QTAIM analysis, a BCP or BP is not observed between tungsten and C\textsubscript{\textbeta} for any of the tungstenacyclobutadienes listed in Fig. 2. All of them showed a characteristic ring critical point (RCP) for the metallacycle. The QTAIM molecular graphs given for the optimized geometries of WEMYUK and CUYJEL in Fig. 3 along with contours of the Laplacian of electron density are useful to understand the typical electron density features of the metallacyclobutadiene. Very similar molecular graphs have been obtained for all other systems (ESI\textsuperscript{†}). As seen in these molecular graphs, at the RCP, the four ring paths coming from the surrounding four BCPs do not meet sharply as expected for a normal ring structure. Instead, the RCP can be considered as an indication of bonding interaction between the metal and C\textsubscript{\textbeta}. Thus the presence of a catastrophe critical point can be considered as an indication of bonding interaction between the metal and C\textsubscript{\textbeta}. In Table 2, the three eigenvalues of the catastrophe RCP are given. Since the RCP is designated as a (3, +1) critical point, one of the eigenvalues has to be negative and the other two have to be positive. As we can see, one of the positive eigenvalues is very close to zero (eigenvalue 2) which can be considered as an indicator of the catastrophe nature of the RCP. Hence, the system that shows the lowest positive eigenvalue must have the highest catastrophe character. The smallest positive eigenvalue may become negative with sufficiently strong interaction between W and C\textsubscript{\textbeta} which will give rise to a (3, −1) BCP critical point.

In Fig. 4, the variation of the eigenvalues with a change in the WC\textsubscript{\textbeta} bond distance for various optimized crystal structures is presented. The linear plots given in this figure clearly suggest that with the increase in the WC\textsubscript{\textbeta} interaction, the most positive eigenvalue (eigenvalue 3) becomes more positive, the least positive eigenvalue (eigenvalue 2) becomes smaller while the magnitude of the negative eigenvalue (eigenvalue 1) remains almost constant. On the basis of this figure, we can assume that among all the structures, CUYJEL has the highest amount of 1,3-MC bonding character. By extrapolating the eigenvalue plots in Fig. 4, a value of \textasciitilde1.98 Å for WC\textsubscript{\textbeta} distance can be suggested at which the system may show a BCP along with a clear BP between W and C\textsubscript{\textbeta}. To check this, we reduced the WC\textsubscript{\textbeta} distance of CUYJEL manually and at a distance of 1.99 Å (a saddle point in the potential energy surface); a clear BCP was found along with a BP connecting W and C\textsubscript{\textbeta} (ESI\textsuperscript{†}). Thus it is apparent that the absence of a BCP does not indicate the absence of a bonding interaction. Molecular orbital pictures of WEMYUK given in the ESI\textsuperscript{†} prove that the 1,3-MC interaction mainly arises from significant d\textsubscript{\textalpha}–p\textsubscript{\textbeta} interaction between W and C\textsubscript{\textbeta}.

Among the QTAIM parameters given in Table 2, the most important in the analysis of the 1,3-MC bond are those associated with the catastrophe RCP. The \( \rho \) at the RCP is in the range

### Table 2. QTAIM parameters calculated for the WCBD systems and the ‘deproti’ metallacycle CEGGAW

<table>
<thead>
<tr>
<th></th>
<th>QTAIM parameters (au)</th>
<th>Eigenvalue at RCP (au)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>WC\textsubscript{\textalpha} BCP</td>
<td>C\textsubscript{\textbeta} BCP</td>
</tr>
<tr>
<td>WEMYIY</td>
<td>0.230 0.271 0.126</td>
<td>−0.108 0.071 0.417</td>
</tr>
<tr>
<td>WEMYOE</td>
<td>0.232 0.272 0.129</td>
<td>−0.111 0.070 0.421</td>
</tr>
<tr>
<td>WEMYUK</td>
<td>0.232 0.270 0.127</td>
<td>−0.109 0.071 0.416</td>
</tr>
<tr>
<td>COMREB</td>
<td>0.226 0.274 0.125</td>
<td>−0.109 0.071 0.406</td>
</tr>
<tr>
<td>CONISH</td>
<td>0.232 0.272 0.132</td>
<td>−0.115 0.064 0.428</td>
</tr>
<tr>
<td>CUYJEL</td>
<td>0.226 0.276 0.139</td>
<td>−0.125 0.047 0.459</td>
</tr>
<tr>
<td>KISGID</td>
<td>0.219 0.274 0.116</td>
<td>−0.099 0.079 0.379</td>
</tr>
<tr>
<td>CEGGAW</td>
<td>0.218 0.297 0.176\textsuperscript{a}</td>
<td>−0.197\textsuperscript{a} −0.020\textsuperscript{a} 0.485\textsuperscript{a}</td>
</tr>
</tbody>
</table>

\( a \) Values correspond to WC\textsubscript{\textbeta} BCP.

![Fig. 3](image-url) Molecular graphs of WEMYUK and CUYJEL, showing a flat curvature for the meeting point of ring paths along the contours of the Laplacian of electron density. Only the metallacycle region is shown for clarity and \( \rho \) values are in au.
0.116–0.139 au. This indicates a significant buildup of electron density between W and C. In the case of the ‘deproti’ metallacycle CEGGAW, a BCP is observed between W and C with a ρ value of 0.176 au. This can be considered as a well-defined 1,3-MC bond in a metallacycle. Although the Cρ of CEGGAW is tri-coordinate, the ρ value of its WCρ bond is useful to compare the strength of the 1,3-MC bond of the WCBD. The WCBD systems are 20–34% smaller than the BCP ρ value of CEGGAW and this indicates that the 1,3-MC interaction in the former is proportionally weaker than the latter. In all the metallacycles reported in Table 2, WCα and CαCβ bonds possess some amount of double bond character as their BCP ρ values show significantly higher values than a typical WC single bond (0.165 au) and a typical CC single bond (0.240 au).

Among all the WCBD structures given in Fig. 2, a Cα-H bond is present only in CUYJEL and this system showed the highest ρ value at the catastrophe RCP. Schrock et al. have reported the removal of alcohol from this system, leading to the formation of ‘deproti’ metallacycles.69 The optimised structure of the ‘deproti’ metallacycle of CUYJEL is an energy minimum and in the QTAIM analysis this molecule showed a clear BCP with a ρ value of 0.175 au for the WCρ bond of length 2.074 Å (ESI†).

### Bond order analysis

The bond order parameters depicted in Table 3 strongly augment the conclusions drawn from the structural data and QTAIM analysis that tungsten is bonded to Cβ for the 1,3-WC bonding. All the WCBD structures show a WCρ bond order in the range 0.286–0.422, which suggests significant bonding interaction between W and C. The CUYJEL system composed of an alkoxide ligand has the highest WCρ bond order of 0.422. KISGID with an imidazolin iminato ligand has the smallest WCρ bond order of 0.286 whereas the pincer ligand incorporated structures of Veige et al. show a WCρ bond order of ~0.35.

### 13C-NMR analysis

Schrock et al. proposed the use of 13C-NMR chemical shift as a measure of WCρ interaction in the case of metallacyclobutane intermediates of alkyne metathesis.70 A similar 13C-NMR analysis has been used by Romero and Piers to prove the formation of a ruthenacyclobutane intermediate in the Grubbs alkene metathesis mechanism, as the differences in the chemical shifts observed for the Cα and Cβ were very large.71 Very recently we have shown that such behaviour can be attributed to the unusual penta-hypercoordinate bonding character of Cβ in the MCB.65 In this work, the structure of interest is MCBD. Because of the unusual pC bonding character of Cβ, a large difference in the chemical shift values of Cα (δCα) and Cβ (δCβ) is expected for MCBD. This is indeed true and in all the cases, the NMR signal of Cβ is 52–79 ppm smaller than that of Cα (Table 4), which is in agreement with the experimental data (ESI†). The 1,3-MC bonding shields the Cβ more than Cα leading to a more upfield shift for Cβ than for Cα. We propose that the large difference in the 13C-NMR values of Cα and Cβ can be considered as a signature of 1,3-MC bonding in the metallacycle.

The elucidation of the crystal structures of several MCBD systems of alkyne metathesis clearly suggests that they possess superior stability compared to the 4-membered anti-aromatic cyclobutadiene.72 It is well known that anti-aromatic to aromatic transformation of organic moieties can be obtained by the incorporation of a transition metal center via the chelating effect.73,74 The aromatic character of such systems is known as metalloaromaticity.75 Erdman and Lawson76 studied metalloaromaticity in tungstenacyclobutadiene using computational techniques and reported that the nucleus independent chemical shift at the ring center, NICS(0), is ~28 ppm for the Schrock’s MCBD crystal, BONXOR. The high negative NICS(0) value suggested aromatic stabilization of the MCBD. Apart from NICS(0), NICS at 1 Å above the ring center, NICS(1) and its zz-tensor component NICS(1)zz have also been used for the study of the aromatic nature of a molecule. In Table 5, the NICS(0), NICS(1) and NICS(1)zz of all the complexes are reported which may be compared with those of benzene (NICS(0) = −7.8, NICS(1) = −10.8 and NICS(1)zz = −28.1), a reference for a typical aromatic molecule. NICS(0) in the range of −26 to −30 ppm is close to the value reported by Erdman and Lawson for BONXOR and indicates the strong metalloaromatic character of these systems. The high negative values of NICS(1) and NICS(1)zz compared to benzene also indicate the substantial stabilization of the former due to metalloaromaticity.

Very recently the Herges group developed a methodology to calculate the anisotropy of induced current density (AICD)

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**Table 3** Wiberg bond order calculated for MCBD in the optimized geometries of MCBD

<table>
<thead>
<tr>
<th>MCBD</th>
<th>WCα</th>
<th>WCα</th>
<th>CαCρ</th>
<th>CαCρ</th>
<th>WCρ</th>
</tr>
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<tbody>
<tr>
<td>WEMYIY</td>
<td>1.385</td>
<td>1.356</td>
<td>1.256</td>
<td>1.175</td>
<td>0.348</td>
</tr>
<tr>
<td>WEMYOE</td>
<td>1.386</td>
<td>1.416</td>
<td>1.261</td>
<td>1.181</td>
<td>0.355</td>
</tr>
<tr>
<td>WEMYUK</td>
<td>1.419</td>
<td>1.405</td>
<td>1.220</td>
<td>1.222</td>
<td>0.351</td>
</tr>
<tr>
<td>COMREB</td>
<td>1.511</td>
<td>1.227</td>
<td>1.358</td>
<td>1.082</td>
<td>0.336</td>
</tr>
<tr>
<td>CONISH</td>
<td>1.370</td>
<td>1.450</td>
<td>1.280</td>
<td>1.134</td>
<td>0.395</td>
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<tr>
<td>CUYJEL</td>
<td>1.363</td>
<td>1.430</td>
<td>1.308</td>
<td>1.170</td>
<td>0.422</td>
</tr>
<tr>
<td>KISGID</td>
<td>1.119</td>
<td>1.603</td>
<td>1.473</td>
<td>1.035</td>
<td>0.286</td>
</tr>
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**Table 4** 13C-NMR values calculated for MCBD in the optimized geometries of MCBD

<table>
<thead>
<tr>
<th>MCBD</th>
<th>δCα</th>
<th>δCα</th>
<th>δCβ</th>
<th>δCα–δCβ</th>
</tr>
</thead>
<tbody>
<tr>
<td>WEMYIY</td>
<td>205.3</td>
<td>218.4</td>
<td>144.8</td>
<td>67.1</td>
</tr>
<tr>
<td>WEMYOE</td>
<td>200.4</td>
<td>225.6</td>
<td>152.5</td>
<td>60.5</td>
</tr>
<tr>
<td>WEMYUK</td>
<td>207.0</td>
<td>234.7</td>
<td>147.4</td>
<td>73.5</td>
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<tr>
<td>COMREB</td>
<td>204.4</td>
<td>199.3</td>
<td>144.0</td>
<td>57.8</td>
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<tr>
<td>CONISH</td>
<td>199.6</td>
<td>213.6</td>
<td>154.2</td>
<td>52.4</td>
</tr>
<tr>
<td>CUYJEL</td>
<td>208.6</td>
<td>222.8</td>
<td>137.0</td>
<td>87.7</td>
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<tr>
<td>KISGID</td>
<td>213.7</td>
<td>214.0</td>
<td>134.4</td>
<td>79.4</td>
</tr>
</tbody>
</table>

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maps and used it to quantify and visualize electron delocalization and aromaticity in molecules. The AICD isosurface plot with current density vectors plotted on it gives either diatropic (clockwise) or paratropic (anti-clockwise) circulation of the current density depending on the aromatic or anti-aromatic nature of the molecule. Fig. 5 depicts such plots to visualize aromatic features for two representative cases, viz. WEMYUK and CUYJEL. It is clear from these plots that the MCBD systems possess aromatic delocalization of the π-electrons.

Systems with more than one MCBD

Structural, electronic and bonding analyses of the known WCBD structures confirm that the interaction between W and C_β can be considered as a direct bond. This new WC_β bond generally called the 1,3-MC bond defines the planar tetracoordinate state of C_β. Since several WCBD structures exist in stable form, the 1,3-MC bond which contributes to their stability can be utilized to incorporate _pC centers into organometallic complexes. Although the theoretical exploration of _pC chemistry is advanced to some extent, the realistic application of a system containing _pC centers is yet to be achieved. Our results suggest that the consideration of WCBD systems as _pC systems brings in more options to the design of realistic organometallic systems. To explore this revealing thought, we propose the use of tungstenacyclobutadiene as a basic building block to construct complex organometallic structures containing multiple _pC centers. The structural motif given in Fig. 1b is useful to illustrate the strategies used to develop such expanded systems in 1-, 2- and 3-dimensions and the proposed models are given in Fig. 6.

Assuming the X-direction as the direction of the WC_β bond, extension of the structure in that direction can be envisaged by connecting two WCBD structures similar to the known chloro-ligated Schrock system BONXOR through the β carbon as shown for model 1. In 1, the C_β of the two metallacycles are bonded with a distance of 1.479 Å and the two metallacycles show a symmetric orthogonal arrangement. The WC_β distance of 2.169 Å in 1 is similar to any of the 1,3-WC_β bond distances given in Table 1. Further, the WC_α bond distance of 1.923 Å indicates its double bond character while the CC bond distance of 1.446 Å indicates significant activation of that bond compared to a typical CC double bond (1.33 Å) or a conjugated aromatic CC bond (1.40 Å). We also consider the formation of two 1,3-WC bonded metallacycles around one tungsten atom. This model 2 is a minimum and both metallacycles in this complex show the characteristic 1,3-WC bond distance of 2.152 Å.

Expansion of the metallacyle in the Y-direction (more towards the direction of C_α) leads to the construction of two types of complexes, viz. 3 and 4. 3 is constructed by connecting C_α of two metallacycles whereas, in 4, the C_β of one metallacyle serves as the C_α of the other metallacycle, meaning that a CC bond is shared by both the metallacycles. Rosenthal et al. and many others reported complexes of type 4 and schematics of such structures are reported in the ESI.

<table>
<thead>
<tr>
<th>MCBD</th>
<th>NICS(0)</th>
<th>NICS(1)</th>
<th>NICS(1)_{zz}</th>
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ively for 3 and 4 underlines the presence of 1,3-MC interactions in these complexes.

Polymeric 1-dimensional extension of the dimetallacycles 2–4 is possible while such an extension of 1 has to be compromised due to chloro-ligation. Transition metal acetylide complexes are well discussed in the literature and by using acetylide units to connect metal centers, the linear expansion of 1-type architecture can also be achieved and the model for such a structure is 5.\textsuperscript{79–81} Model 6 is made by connecting two units of 2 via the C\textsubscript{2h}. The one-dimensional extension of 3 is used to construct 7 while such an extension of 4 would lead to the formation of 8. All these structures are energy minima, and all of them show single bond-like WC\textsubscript{β} distances indicating the presence of 1,3-MC bonding. In 7 and 8, the carbon chain resembles that of a polyene chain suggesting that these systems could be even considered as metal-incorporated polyene. All these extended structures preserve the 1,3-MC bonding features of metallacycles.

By combining the expansion patterns shown for the Z- and Y-directions, two-dimensional expansions can be created. For instance, 9 is made by connecting 2 with 5. Similarly, 10 can be made by combining 2 and 6 which can be further extended.
via the α-carbon or β-carbon. All the MCBD units in 9 and 10 possess single bond-like WCβ distances.

Wiberg bond order analysis of the dimetallacycles (Table 6) shows strong WCβ interactions in both WCB regions (0.371–0.477). Model 4 where one CC bond is shared between the two metallacycles showed the highest WCβ bond order of 0.477. The strongest (1.499) and the weakest WCa (0.765) bonds are found in 4. In all the cases, the CC bond order lies between 1.167 and 1.302. QTAIM analysis of these dimetallacycles (Table 6) showed a catastrophe ring critical point, where the ring paths show a flat curvature (ESI†). The ρ value at the catastrophe point is nearly 0.133 au, which is close to a typical WC single bond value. Eigenvalue analyses of these models are discussed in the ESI,† which confirms the catastrophe nature of the RCP.

Negative values for all the three NICS indices (NICS(0), NICS(1) and NICS(1)zz) have been observed for the dimetallacycles 1–4 (Table 7) indicating their metalloaromatic character. 13C-NMR analysis of these molecules showed that α and β carbons are markedly different and suggest the presence of 1,3-MC bonding between metal and Cβ. The QTAIM and NMR features of all the 1-dimensional (5–8) and 2-dimensional (9–10) extended structures are very similar to the dimetallacycles and suggest that Cβ of the WCB region is 1,3-WC bonded and exists in the planar tetracoordinate state.

Further extension of 1- and 2-dimensional structures to 3-dimensional networks is possible through proper α- and β-carbon connectivity (Fig. 7). For example, 11 can be built from two units of 9. Further, complex 12 can be made by combining two units of 9 along with two units of pyrene. As we can see, these types of expansions of the WCB structures can lead to the formation of metal–organic cavities in the system. In the case of 12, a well-defined cavity of size (1.06, 0.81, 0.72 nm) in the (X, Y, Z) directions is clearly seen. The 3-dimensional structures 11 and 12 also possess a single-bond like WCβ distance (~2.2 Å) and all the characteristic QTAIM and NMR features typically seen for a 1,3-WC bonded carbon atom.

### Conclusions

Several tungstenacyclobutadienes available in the CSD have been studied for 1,3-WC bonding interactions. A single bond-like WCβ distance in these complexes is established with a significantly high bond order and the appearance of a catastrophe ring critical point in the QTAIM analysis. Large negative NICS values obtained for these molecules point to
their metalloaromatic character which is underlined with the diatropic ring current observed in the AICD plot. All these structures showed a large difference in the \(^{13}\text{C}-\text{NMR}\) signals of C\(_\alpha\) and C\(_\beta\), which is considered as a characteristic feature of 1,3-WC bonding. Among the crystal structures, the alkoxide ligated complex CUYJEL reported by Schrock et al. showed the strongest WC\(_\beta\) interaction. In a constrained geometry, this model showed a clear bond critical point between W and C\(_\beta\). This extra bonding interaction is further confirmed by molecular orbital analysis, which clearly showed the d\(_{z^2}\)-p\(_\beta\) interaction between tungsten and carbon. The 1,3-WC bonding in these metallacycles forces the C\(_\beta\) to exist in a planar tetra-coordinate state, p\(_{\beta}\)C. Identification of C\(_\beta\) as a p\(_{\beta}\)C center in WCBD paves the way for a new approach to the design of molecules and materials containing multiple p\(_{\beta}\)C centers. Several such molecules have been proposed by extending the WCBD motif in 1-, 2- and 3-dimensions. The presence of the 1,3-WC bond as well as metalloaromaticity in all these systems is established on the basis of the characteristic bond order, the catastrophe ring critical point in QTAIM, \(^{13}\text{C}-\text{NMR}\) values and various NICS indices. The 3-dimensional structures propose the formation of p\(_{\beta}\)C incorporated metal–organic frameworks.

Acknowledgements

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References