Planar Tetracoordinate Carbon in Tungstenacyclobutadiene of Alkyne Metathesis and Expanded Structures
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i  Fig. S1 Optimized structures of BONXOR and CEGGAW

ii Fig. S2 Contour of Laplacian of electron density along with the molecular graph of optimized geometries of crystal structures (ρ values are given in au).

iii Fig. S3 Contour of Laplacian of electron density along with the molecular graph of CEGGAW (only tungstenacyclobutane is shown for clarity and electron densities are given in au).

iv Constrained geometry of CUYJEL

v Fig. S4 Molecular graph of the constrained geometry of CUYJEL at WC_β =1.99 Å showing a fourth BP for the C_β in the QTAIM analysis.

vi Fig. S5 Optimized geometry and Molecular graph of the deprotiometallacycle corresponding to CUYJEL showing a clear WC_β bond

vii Fig. S6 Molecular orbital picture (HOMO -25) showing significant 1,3-WC interaction in WEMYUK due to the overlap of metal d-orbital and p-orbital on C_β (isosurface value of 0.05 is used).

viii Experimental ^13C-NMR values of the WCBD

ix Complexes with more than one MCB unit

x Fig. S7 Molecular drawings of the crystal structures of the complexes containing 4 type architecture

xi Fig. S8 Contour of Laplacian of electron density along with molecular graph of dimetallacycles 1 - 4. Electron density at the critical points is given in au.

xii Fig. S9 Contour of Laplacian of electron density along with molecular graph of extended WCBD systems 5 - 10. Electron density at the critical points is given in au.

xiii Fig. S10 QTAIM topography of the 3-dimensional metal carbon networks (a) 11 and (b) 12.
i. **Fig. S1 Optimised Structure of BONXOR and CEGGAW**

BONXOR is the metallacycle intermediate of alkyne metathesis reported by Schrock et al.\(^1\) this crystal showed a single bond like MC\(\beta\) distance of 2.115 Å. This structure was thoroughly analysed by suresh and Frenking computationally to establish the presence of 1,3-MC bond.\(^2\) CEGGAW is the deprotiometallacycle reported by Schrock et al. and has a formal single bond between W and C\(\beta\).
ii. **Fig. S2** Contour of Laplacian of electron density along with the molecular graph of optimized geometries of crystal structures (ρ values are given in au).
iii. **Fig. S3** Contour of Laplacian of electron density along with the molecular graph of CEGGAW (only tungstenacyclobutane region is shown for clarity and electron densities are in au).

![Contour of Laplacian of electron density along with the molecular graph of CEGGAW](image)

iv. **Constrained geometry of CUYJEL**

To further establish the catastrophe nature of the RCP in the WCBD models, we decreased the WC$_\beta$ distance of CUYJEL manually and optimized the geometry after freezing the W and C$_\beta$ coordinate. Thus obtained geometry is a saddle point in the potential energy surface. At a WC$_\beta$ distance of 1.990Å, a clear BP along with a BCP was located for CUYJEL as given in Fig. S4.

v. **Fig. S4** Molecular graph of the constrained geometry of CUYJEL at WC$_\beta$ =1.99 Å showing a fourth bond path for the C$_\beta$ in the QTAIM analysis.

![Molecular graph of the constrained geometry of CUYJEL at WC$_\beta$ =1.99 Å showing a fourth bond path for the C$_\beta$ in the QTAIM analysis](image)
vi. **Fig. S5** Optimized geometry and Molecular graph of the deprotiometallacycle corresponding to CUYJEL showing a clear $WC_\beta$ bond.

![Optimized geometry and Molecular graph of the deprotiometallacycle corresponding to CUYJEL](image)

vii. **Fig. S6** Molecular orbital (HOMO - 25) showing significant 1,3-WC interaction in WEMYUK due to the overlap of metal d-orbital and p-orbital on $C_\beta$ (isosurface value of 0.05 is used).

![Molecular orbital (HOMO - 25) showing significant 1,3-WC interaction in WEMYUK](image)
viii. **Experimental $^{13}$C-NMR values of the WCBD structures**

The experimental $^{13}$C-NMR values of the crystal structures and calculated gas phase values for the optimized geometries at BP86/def2-tzvpp level of theory are presented in Table S1 for $C_\alpha$ and $C_\beta$ atoms. Both theory and experiment agree to the fact that $C_\alpha$ atoms have significantly large chemical shift than the $C_\beta$ atoms. Though the theory could not reproduce chemical shift values very close to the experiment, the trends in chemical shift difference between $C_\alpha$ and $C_\beta$ values obtained from theory is in close agreement with experiment.

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ix. **Complexes with more than one MCB unit**

Many crystal structures are known containing 4 type moieties (scheme 1). Rosental *et al.* synthesized many such molecules possessing titanium center. These molecules showed significant interaction between Ti and $\beta$-carbon center indicated by the short distance (~ 2.3 Å).$^8$-$^11$

x. **Fig. S7** Molecular drawings of the crystal structures of the complexes containing 4-type architecture.
Fig. S8 Contour of Laplacian of electron density along with molecular graph of dimetallacycles 1 - 4. Electron density at the critical points is given in au.
xii. **Fig. S9** Contour of Laplacian of electron density along with molecular graph of extended WCBD systems 5 - 10. Electron density at the critical points is given in au.
xiii. Fig. S10 QTAIM topography of the 3-dimensional metal carbon networks (a) 11 and (b) 12.
xiv. Eigenvalues at the catastrophe RCP of dimetallacycles 1 – 4

Eigenvalues at the catastrophe RCP is analyzed to understand the intensity of 1,3-WC interaction in dimetallacycles. Among the three one value is negative and other two are positive. Among the two positive values, one (eigenvalue 2) is close to zero compared to other (eigenvalue 3). Recently we have discussed the analysis of eigenvalue to understand the strength of 1,3-MC interaction. Larger the eigenvalue 3 and smaller the eigenvalue 2 greater is the interaction.

Table S2. Eigenvalue at the catastrophe RCP of dimetallacycles in au

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xv. Cartesian coordinates of optimized geometries of the models studied are given below. All geometries are characterized by zero imaginary frequencies in the vibrational frequency analysis.

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References