

An experimental electron density study on “1-zirconacyclopent-3-yne”†

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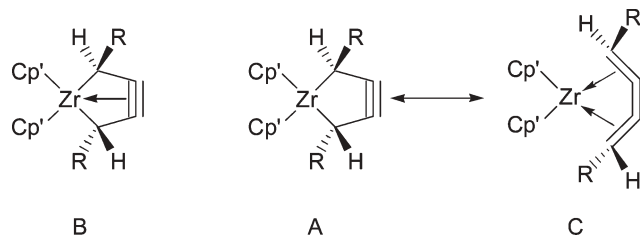
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An electron density analysis of the 1-zirconacyclopent-3-yne complex has been carried out based on X-ray diffraction data, showing that the coordination mode of the but-2-yne-1,4-diyl ligand to the metal is a resonance hybrid between η^2 - σ , π -coordination, as the major contributor, and η^4 - π , π -coordination.

In general, small cyclic alkynes are unstable and difficult to isolate.¹ Five-membered cyclic alkynes, cyclopentynes, are so reactive that they had been only detected spectroscopically,² or by subsequent chemical reaction, such as a 2 + 2 cycloaddition,³ or metal complexation.⁴

We recently reported the synthesis and structure of the zirconocene complexes of 1,2,3-butatriene, and that they could be considered to be five-membered metallacyclic alkynes, *i.e.* 1-zirconacyclopent-3-yne (eqn. (1)).⁵ Surprisingly, the complexes could be isolated and were stable in the solid state at room temperature. The molecular structure of the zirconacyclic complexes was determined using X-ray diffraction, as well as the titanium⁶ and hafnium⁷ complexes, and the short bond distances between these two quaternary carbons (1.21–1.23 Å) suggested a 1-metallacyclopent-3-yne structure. Various spectroscopic data also supported the sp-character of the quaternary carbons. A few theoretical studies on the structure of these unique complexes have appeared. Jemmis and coworkers suggested electron donation from the triple bond to the metal increases the stability of this compound (Form B in Scheme 1).⁸ On the other hand, Lin and Lam proposed a contribution of a η^4 - π , π -coordinated structure (Form C in Scheme 1).⁹ Thus, it is intriguing to collect experimental data on the structure of these complexes. Here, we report on an experimental electron density analysis of the 1-zirconacyclopent-3-yne complex using X-ray diffraction, which provides valuable information on the bonding mode of these unique molecules. To analyze the electron density distribution of the outer shells of the atoms in particular, the data must be highly

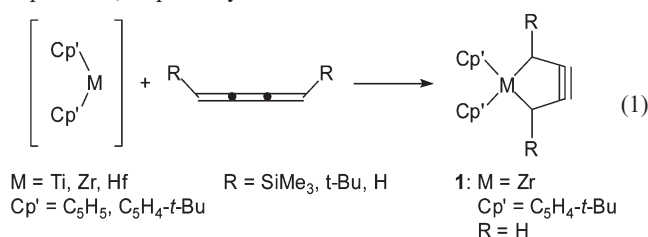


Scheme 1 The suggested bonding mode of the 1-zirconacyclopent-3-yne compound.

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accurate, with a higher resolution than for conventional structural analysis. To achieve this, we collected new diffraction data of **1** using synchrotron radiation, although the structure of **1** has been reported previously utilizing a laboratory Mo-K α X-ray source.⁵ The data were analyzed using a multipole expansion method.‡§ Here, the carbon atoms of the 1-zirconacyclopent-3-yne moiety are abbreviated as C(α) and C(β) for atoms at 2- and 5-, and 3- and 4-positions, respectively.



The structural features of **1** are essentially the same as those described in previous work.⁵ The 1-zirconacyclopent-3-yne moiety is planar within 0.0050(16) Å, and two *tert*-butyl-cyclopentadienyl ligands coordinate to the Zr atom from both sides of the plane with a pseudo-tetrahedral geometry (Fig. 1). The C(β)–C(β) bond (1.250(3) Å) is significantly longer than that determined using conventional X-ray analysis (1.237(3) Å).⁵ Owing to the influence of the densely populated bonding electrons of the C(β)–C(β) triple bond, the corresponding bond lengths from conventional X-ray analysis are apparently shorter than in the real structure. Since the parameters for the bonding electrons and the core electrons are well separated, the C(β)–C(β) bond length in this work is nearer to reality than that from conventional analyses. The bond distances and angles in the 5-membered ring are in good accord with those

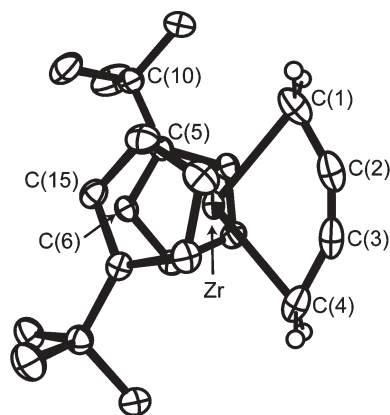


Fig. 1 A view of the molecular structure of **1** drawn with geometric parameters after multipole expansion refinements with an atom-labeling scheme. The displacement ellipsoids are drawn at the 50% probability level. The hydrogen atoms of the Cp' moieties are omitted for clarity. The structure is essentially the same as found in our previous work.⁵

Table 1 The experimental geometric parameters of **1**, and a comparison with values from DFT studies

	Present work	Ref. 8	Ref. 9
		<i>Distance/Å</i>	
Zr–C(1)	2.4193(15)	2.440	2.493
Zr–C(2)	2.3181(15)	2.330	2.328
Zr–C(3)	2.3169(15)	2.330	2.328
Zr–C(4)	2.4361(15)	2.440	2.493
C(1)–C(2)	1.409(3)	1.424	1.407
C(2)–C(3)	1.250(3)	1.259	1.250
C(3)–C(4)	1.413(3)	1.424	1.407
		<i>Angle/°</i>	
C(1)–C(2)–C(3)	150.97(14)	151.2	153.9
C(2)–C(3)–C(4)	151.80(14)	151.2	153.9

from DFT calculations by Jemmis and coworkers,⁸ and Lin and Lam⁹ (Table 1). As reported previously, the Zr⋯C(β) distances are shorter than that of the Zr–C(α) bond. Both Jemmis and coworkers, and Lin and Lam referred to the short distance between the Zr and C(β) atoms, and concluded that the structure of the 1-zirconacyclopent-3-yne is not a mere η²-σ, σ-structure (Form A). Although both groups derived almost the same structure from their calculations, quite different results were asserted. To clarify the bonding mode, it is essential that the interaction between the metal and ligand is investigated.

Fig. 2 shows different sections of the Laplacian maps focused on the 1-zirconacyclopent-3-yne moiety, based on the experimental electron density distribution. The map shows similar features to that of the DFT calculation of Lin and Lam, in particular, those around the metal center. Although Jemmis and coworkers only reported the molecular orbital map,⁸ this seems to show essentially the same features of the total electron density distribution as our results do. The valence shell charge concentration (VSCC) on the C(α) atoms extend towards the regions of charge depletion around the Zr atom along the bond directions (Fig. 2(a) and 2(b)). The features of the electron distribution clearly indicate σ-coordination of the C(α) atoms to the Zr atom. The distribution also implies a trace π-bonding character of the C(α)–C(β) bonds. The VSCCs on the C(α)

atoms slightly increase along the Zr–C(α) bond directions, and are spread over the C(α)–C(β) bonds, rather than being localized on the C(α) atoms. These show that a small portion of the p-electron on the C(α) atom is delocalized over the C(α)–C(β) bond in the 1-zirconacyclopent-3-yne plane. This delocalization brings about the π-bonding in the C(α)–C(β) bonds, namely the ‘in-plane’ π-bonding, suggesting a slight contribution of a η⁴-π, π-coordinated structure (Form C) to the Zr–C(α) bond. In addition, as shown in Fig. 2(c), the VSCC at the center of the C(β)–C(β) bond deforms vertically to the 1-zirconacyclopent-3-yne plane. This feature of the VSCC clearly indicates an ‘in-plane’ π-delocalization of the C(β)–C(β) bond over the C(α)–C(β) bonds. The delocalization of the π-electrons over the but-2-yne-1,4-diyl ligand varies bond distances of the ligand from those of the localized structure (Form A): the C(α)–C(β) bonds are shortened, and the C(β)–C(β) bond is elongated. We consider the complex corresponds to that suggested by Lin and Lam, where the complex is a resonance hybrid between the η²-σ, σ- (Form A) and η⁴-π, π-coordinated structures (Form C). We also tried to account for our results based on Form B. However, this structure cannot fully explain our results, in particular, the shortening of the C(α)–C(β) bonds.

To evaluate the interaction between the Zr and but-2-yne-1,4-diyl ligand quantitatively, a topological analysis was applied to the total electron density distribution. The bond critical points and bond paths are observed on the Zr–C(α) bond, as well as for all bonds of the ligands and the bondings of Zr-cyclopentadienes (Fig. 3). These were not found between the Zr and C(β) atoms, and the Zr and the C(β)–C(β) bond. In addition, no deformation of π-electrons on the C(β)–C(β) bond towards the Zr atom was observed (Fig. 2(c)). These results strongly support the σ-coordination of the C(α) atoms to the Zr atom without the π-donation of the C(β)–C(β) bond (Form A). The absence of bond critical points between the Zr and C(β) atoms and/or the C(β)–C(β) bond, and the π-electron distribution on the C(β)–C(β) bond clearly shows an absence of any interatomic interaction between them. If anything, the interaction must be negligibly small. The values of ρ(r_{bcp}) and ∇²ρ(r_{bcp}) are listed in Table 2 for the Zr–C(α), the C–C bonds of

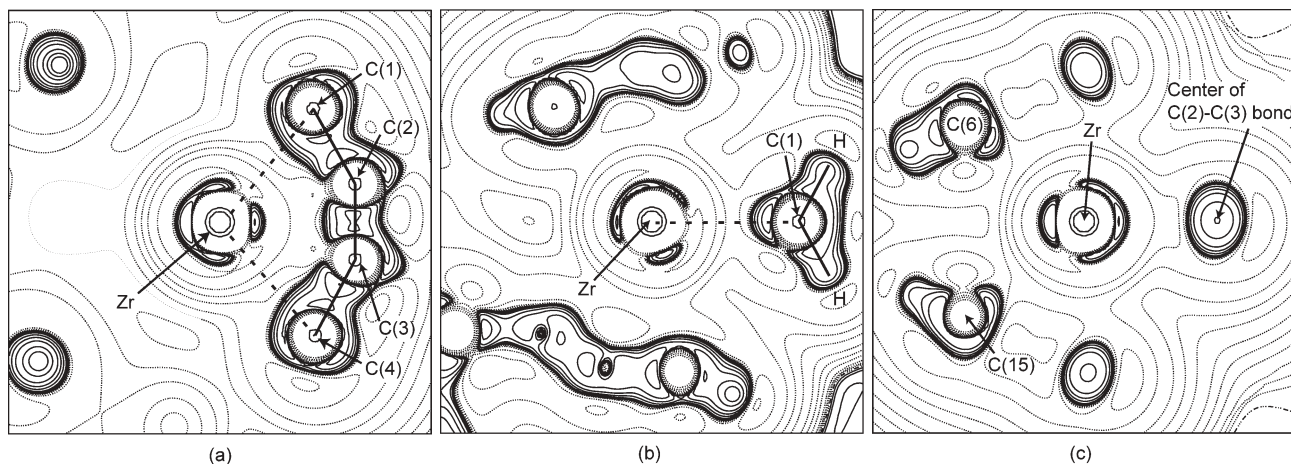


Fig. 2 Laplacian distribution plots of (a) the plane defined by the Zr, C(1), and C(4) atoms, (b) the cross section of the Zr–C(1)–C(4) plane containing the Zr–C(1) bond, and (c) the cross section of the Zr–C(1)–C(4) plane passing through the Zr atom and the center of the C(2)–C(3) bond. The dotted contours denote positive values of ∇²ρ(r), the solid lines denote negative values of ∇²ρ(r), and the broken lines in (a) and (b) denote the Zr–C(α) bonds. Positive and negative contours indicate regions of local charge depletion and concentration, respectively. The contours are drawn at ±2 × 10ⁿ, ±4 × 10ⁿ and ±8 × 10ⁿ (where n = –2, –1, 0, 1, 2) e Å^{–5}.

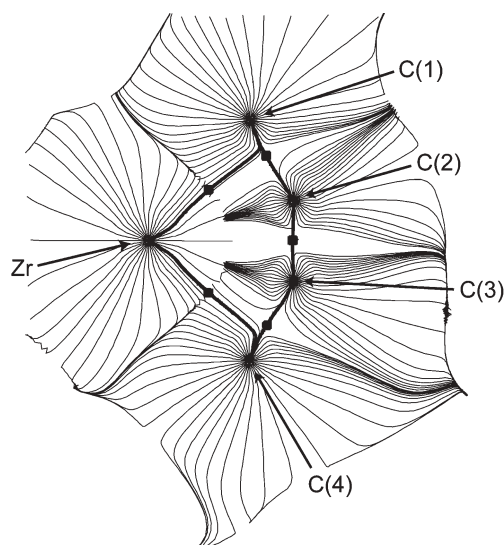


Fig. 3 Gradient trajectories (fine lines), bond paths (bold lines) and bond critical points (filled squares) in the plane defined by Zr, C(2) and C(3). The bond paths of the Zr–C(α) bonds curve inwardly with respect to the 1-zirconacyclopent-3-yne ring. These indicate that the ‘in-plane’ π -coordination of the C(α)–C(β) bond contributes to the Zr–C(α) bond.

Table 2 Topological analysis of the bond critical points in ρ

	${}^a \rho(\mathbf{r}_{\text{bcp}})/\text{e } \text{\AA}^{-3}$	${}^b \nabla^2 \rho(\mathbf{r}_{\text{bcp}})/\text{e } \text{\AA}^{-5}$	${}^c \lambda_1'/\text{e } \text{\AA}^{-5}$	${}^c \lambda_2'/\text{e } \text{\AA}^{-5}$	${}^c \lambda_3'/\text{e } \text{\AA}^{-5}$	d_ε
Zr–C(1)	0.36	4.4	–1.3	–0.8	6.5	0.64
Zr–C(4)	0.35	4.5	–1.3	–0.8	6.6	0.68
Zr–C(6)	0.28	3.4	–1.0	–0.3	4.7	2.4
Zr–C(15)	0.28	3.4	–1.1	–0.3	4.8	2.2
C(1)–C(2)	2.09	–18.3	–13.5	–11.7	6.9	0.16
C(2)–C(3)	2.97	–40.9	–23.1	–19.8	2.0	0.17
C(3)–C(4)	2.16	–20.8	–14.4	–12.5	6.1	0.15
C(5)–C(6)	1.99	–14.9	–13.9	–11.5	10.5	0.21
C(5)–C(10)	1.77	–12.4	–11.1	–10.9	9.5	0.02

^a $\rho(\mathbf{r}_{\text{bcp}})$ indicates the electron density at the bond critical points. ^b $\nabla^2 \rho(\mathbf{r}_{\text{bcp}})$ indicates the Laplacian of the electron density at the bond critical points. ^c λ_i denotes the eigenvalues of the Hessian matrix of $\rho(\mathbf{r}_{\text{bcp}})$. ^d ε is the bond ellipticity, $\varepsilon = \lambda_1/\lambda_2 - 1$.

the but-2-yne-1,4-diyl ligand and some Zr–Cp' bonds. A comparison of these values for the Zr–C(α) bonds with those of the Zr–Cp' bond shows that the Zr–C(α) bonds are stronger than the Zr–Cp' bonds. A trace of the π -bonding component between the C(α)–C(β) bond and the Zr atom was also shown by our topological analysis. As shown in Fig. 3, the bond paths of the Zr–C(α) bonds curve inwardly near the C(α) atoms. These curved paths clearly show the contribution of the π -coordination of the C(α)–C(β) bond to the Zr–C(α) bond. In addition, a significantly large value of ε of the Zr–C(α) bonds was observed, but this was smaller than that of the Zr–Cp' bonds, which also indicates a contribution of the π -coordination. The partial delocalization of the π -electrons in the but-2-yne-1,4-diyl ligand is also suggested by the larger ε value of the corresponding C–C bonds. The contribution of the π -coordination however, must be small, since the bond paths and bond critical points were not found between the Zr and C(β) atoms.

In conclusion, we have analyzed the bonding of **1** based on the experimental electron distribution. The topology of the electron

density distribution reveals that the coordination of the but-2-yne-1,4-diyl ligand to the Zr atom in the 1-zirconacyclopent-3-yne system is a resonance hybrid between the η^2 - σ , σ - and η^4 - π , π - coordinations. The major contributor is the η^2 - σ , σ - coordination, while the contribution of the η^4 - π , π - coordination is small. These results are in agreement with our previous studies based on spectroscopic analysis and hydrolysis reactions.⁵

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Notes and references

‡ Diffraction data of **1** were collected at 106 K with a Rigaku Mercury CCD diffractometer installed at KEK PF-AR NW2 beam line. Wavelength of X-rays was adjusted to 0.7000 Å. The reported structure was used as an initial structure. Following high order refinements by the SHELXL-97¹⁰ program using all reflections with $\sin\theta/\lambda \geq 0.6 \text{ \AA}^{-1}$, the total electron density distribution was fitted using the multipole model using the reflections with $I \geq 1.5\sigma(I)$, $\sin\theta/\lambda \leq 0.8 \text{ \AA}^{-1}$, according to the Hansen and Coppens formalism¹¹ as implemented in the XD program package.¹² Multipole parameters for Zr, C and H atoms were refined up to hexadecapole, octupole and dipole levels, respectively. Chemical constraints were applied by assuming C_2 symmetry.

§ Crystal data for $C_{22}H_{30}Zr$, $M = 385.68$, monoclinic, $a = 26.6682(4)$, $b = 8.8160(1)$, $c = 8.1534(1) \text{ \AA}$, $\beta = 90.8516(5)^\circ$, $U = 1916.71(4) \text{ \AA}^3$, $T = 106 \text{ K}$, space group $P2_1/n$ (no. 14), $Z = 4$, $\mu(0.7000 \text{ \AA}) = 0.552 \text{ mm}^{-1}$, 22754 reflections measured, 13327 unique ($R_{\text{int}} = 0.040$) up to $(\sin\theta/\lambda)_{\text{max}} = 1.0 \text{ \AA}^{-1}$, in which 6915 reflections with $I \geq 1.5\sigma(I)$ and $(\sin\theta/\lambda)_{\text{max}} = 0.8 \text{ \AA}^{-1}$ were used in multipole expansion refinements. The final $R(F) = 0.0239$ ($I \geq 1.5\sigma(I)$) and 0.0400 (all data). CCDC 290015. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b516229g.

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