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Photochemical Synthesis of a Zirconium Cyclobutadienyl Complex†

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Photolysis of $(^{\text{Me}}\text{PMP}^{\text{Me}})_2\text{ZrBn}_2$ ($^{\text{Me}}\text{PMP}^{\text{Me}}$ = 3,5-dimethyl-2-(2-pyridyl)pyrrolide) in the presence of diphenylacetylene yields the first η^4 -cyclobutadienyl zirconium complex, $(^{\text{Me}}\text{PMP}^{\text{Me}})_2\text{Zr}(\eta^4\text{-C}_4\text{Ph}_4)$, through formal [2+2] cycloaddition of two alkynes at a putative low-valent zirconium intermediate. This unique reactivity expands the scope of alkyne coupling reactions at low-valent zirconium centers that traditionally produce zirconacyclopentadienes.

The intrinsically high reactivity of reduced early transition metal compounds makes them attractive targets for the development of new stoichiometric and catalytic transformations that often offer orthogonal reactivity patterns compared to late transition metals.¹ Photochemical generation of these low-valent intermediates using visible light under otherwise mild reaction conditions provides a convenient alternative to the more common use of strong reducing agents. Photolysis of organometallic group 4 complexes can provide access to low valent group 4 species via M-C bond cleavage.² This reactivity was first documented in the photolytic decomposition of tetraalkyl zirconium compounds more than four decades ago^{3,4} and was subsequently expanded to more controlled reactions involving dicarbonyl, dialkyl, and diaryl zirconocene species albeit mostly using UV radiation.^{5–8} While the highly pyrophoric organometallic products of these photolysis reactions eluded definitive characterization in the absence of additional substrates, photochemical reactions in the presence of alkynes resulted in the facile formation of metallacyclopentadienes (M = Ti, Zr, Hf) via reductive alkyne coupling at a putative low valent M^{II} center.^{6,9} Renewed interest in photochemical Zr-C bond activation has been sparked in recent years. The strong reducing power of the proposed Zr^{III} or Zr^{II} intermediates has

been harnessed to facilitate the alkali metal-free formation of zirconocene complexes with highly reduced N₂ ligands¹⁰ and for the activation of inert aryl C-F bonds.¹¹ Photochemical activation of Zr-C and Zr-P bonds by visible light irradiation has been utilized in radical cyclization-allylation¹² and hydrophosphination reactions,^{13,14} respectively. Recently, Agapie et al. showed that a photochemically generated reduced zirconium centre can be stabilized by a redox noninnocent pendant anthracene ligand and serves as a masked Zr^{II} equivalent in stoichiometric [2+2+1] cycloaddition of alkynes with carbon monoxide to yield cyclopentadienones and the catalytic [2+2+2] reaction of alkynes and nitriles producing pyrimidines.¹⁵

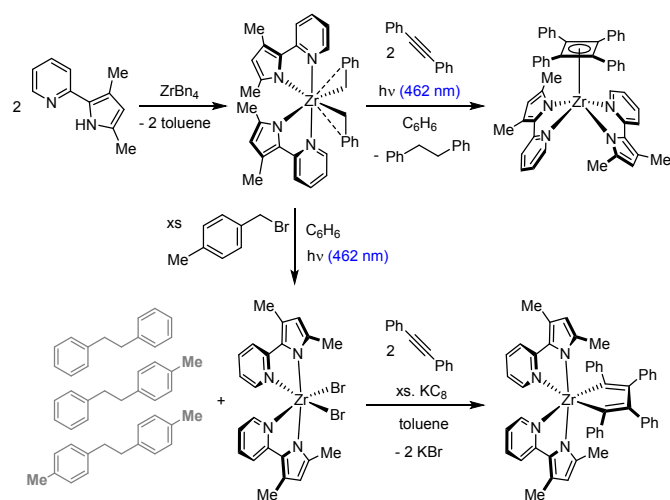
As part of our ongoing investigations of photoactive zirconium complexes, we recently reported facile light-induced C-C bond formation in a zirconium complex with two 2-phenyl-6-(pyrrol-2-yl)pyridine ligands.¹⁶ While low-valent intermediates were not directly observable, reactions in the presence of mild oxidants such as benzyl bromide or dibenzyl disulfide produced the corresponding zirconium dibromide and bis-sulfido adducts in near quantitative yields and remarkable purity. One advantage of these reactions compared to the previously discussed zirconocene examples is the use of visible light rather than UV radiation, which is the likely reason for the excellent selectivity of our photochemical transformations. The improved optical properties can be attributed to the presence of electron-rich pyridine monopyrrolate (PMP) ligands that allow for lower energy ligand-to-metal charge transfer (LMCT) transitions within the transition metal chromophore.^{16,17} Here we describe the successful extension of this design strategy to $(^{\text{Me}}\text{PMP}^{\text{Me}})_2\text{ZrBn}_2$ ($^{\text{Me}}\text{PMP}^{\text{Me}}$ = 3,5-dimethyl-2-(2-pyridyl)pyrrolide), for which the C-C coupled organic product bibenzyl can leave the coordination sphere of the complex to allow for additional reactivity. Photolysis in the presence of diphenylacetylene results in the selective formation of an unprecedented zirconium cyclobutadienyl complex.

The reaction of two equivalents of H^{Me}PMP^{Me} with tetrabenzylzirconium resulted in clean formation of intense orange $(^{\text{Me}}\text{PMP}^{\text{Me}})_2\text{ZrBn}_2$ (Scheme 1). The molecular structure

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established by single crystal X-ray diffraction (Figure 1) revealed two η^2 -bound benzyl ligands as indicated by the small Zr-CH₂-CPh angles (92.76(11)° and 94.89(11)°) and short Zr-CPh distances (2.809(2) Å and 2.839(2) Å). The ¹H NMR spectrum of (MePMPMe)₂ZrBn₂ in benzene-*d*₆ is consistent with the solid state structure and indicates a C₂-symmetric molecule in solution. Variable-temperature (VT)-NMR spectra revealed a dynamic process associated with the η^2 -benzyl ligands (Figure S6). Below 10 °C, two well-resolved doublets can be observed for the diastereotopic benzylic protons indicating a static structure with η^2 -bound ligands on the NMR timescale. At higher temperatures, the two signals broaden and coalesce (T_c = 40 °C) into a single resonance for four magnetically equivalent protons. The energy barrier for this process was estimated as $\Delta G^\ddagger = 14.6$ kcal mol⁻¹ and suggests that the complex samples several different conformations of the benzyl ligands at and above room temperature in solution.



Scheme 1. Synthetic pathways reported in this work.

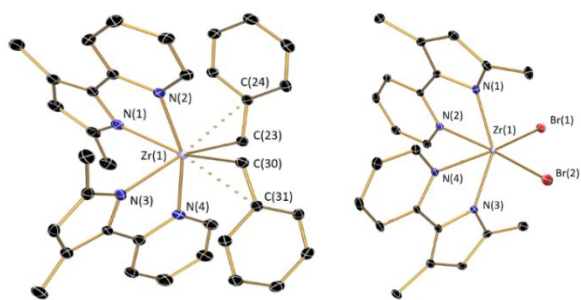


Figure 1. Representation of the molecular structure of (MePMPMe)₂ZrBn₂ (left) and (MePMPMe)₂ZrBr₂ (right) with 30% probability ellipsoids. Hydrogen atoms have been omitted for clarity.

The electronic absorption spectrum of (MePMPMe)₂ZrBn₂ (Figure 2) exhibits a single broad absorption band with a maximum at 415 nm ($\epsilon = 12,300$ M⁻¹ cm⁻¹). Two additional, overlapping features with significantly higher absorptivity can be observed in the UV region of the spectrum. Time-dependent density functional theory (TD-DFT) calculations were performed to elucidate the nature of the electronic transitions but show only moderate agreement with the

experimental spectrum (Figure 2). Most notably, the single broad absorption feature in the visible region observed experimentally is split into two distinct signals in the same wavelength range in the computed spectrum. This discrepancy likely arises from the fact that the calculations are based on an optimized structure with well-defined, static Zr benzyl interactions, while the experimental data envelopes an ensemble of conformations and their associated spectra due to the dynamic behaviour of the benzyl ligands in solution established by NMR spectroscopy. With this caveat in mind, a more detailed analysis of the two calculated absorption bands revealed contributions from several energetically close-lying excited states. The molecular orbitals acting as donor orbitals were identified as HOMO and HOMO-1 (pyrrole π -system) as well as HOMO-2 and HOMO-3 (Zr-C σ -bonds). The acceptor orbitals were found to be LUMO to LUMO+2 and exhibit significant Zr character of 30-60%. The participation of the Zr benzyl σ -bonds in these optical transitions supports the hypothesis that the orientation of the benzyl ligands strongly influences the spectral features. The molecular orbital analysis suggested that visible light excitation should facilitate Zr-C bond homolysis with concomitant reduction of the metal by transferring electron density from the primarily carbon-centred Zr-C σ -bonds to orbitals with higher Zr character.

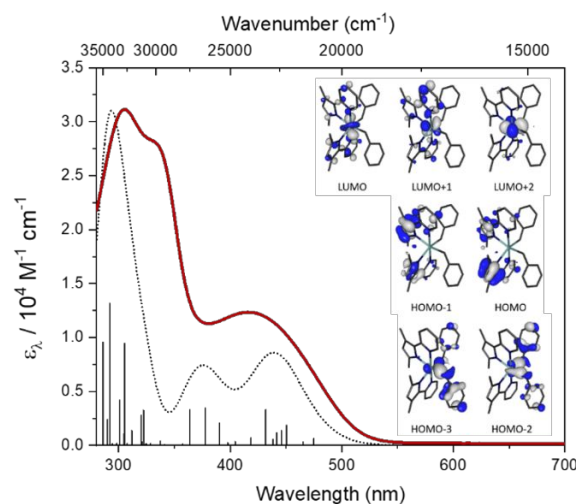


Figure 2. Electronic absorption spectrum of (MePMPMe)₂ZrBn₂ recorded in benzene solution at room temperature (red) and TD-DFT predicted spectrum (dotted black, fwhm 2000 cm⁻¹). Vertical bars indicate the position of the predicted transitions. Inset: Frontier molecular orbitals of (MePMPMe)₂ZrBn₂ contributing to the predicted transitions between 350-500 nm.

Consistent with this hypothesis, irradiation of benzene solutions of (MePMPMe)₂ZrBn₂ with blue light (LED, $\lambda_{\text{max}} = 462$ nm) in the presence of excess diphenylacetylene resulted in formation of a single new zirconium species with one equivalent of bibenzyl as the only by-product. Complete conversion of (MePMPMe)₂ZrBn₂ occurred within minutes exhibiting clean first-order kinetics with respect to irradiation time, which was established by intermittent irradiation experiments (Figure S23). ¹H NMR spectroscopy signalled

incorporation of two equivalents of diphenylacetylene into the new Zr complex. However, the number of resonances associated with the phenyl groups was inconsistent with the formation of a zirconacyclopentadiene moiety traditionally formed in the reaction of low valent zirconium intermediates with alkynes^{18–24} and indicated four equivalent phenyl substituents. Crystallographic analysis of a single crystalline sample established the formation of the half-sandwich complex $(\text{MePMP}^{\text{Me}})_2\text{Zr}(\eta^4\text{-C}_4\text{Ph}_4)$ shown in Figure 3. The compound can formally be described as containing an η^4 -bound cyclobutadiene ligand resulting from [2+2] cyclization of two diphenylacetylene molecules. The structure is best described as a four-legged piano stool complex with a pseudo-square pyramidal coordination environment around the zirconium centre. The two MePMP^{Me} ligands form the base of the square pyramid placing the two pyrrolide units in *trans*-position to each other. The cyclobutadiene ligand forms a nearly perfect square with C-C-C angles between $88.1(4)^\circ$ and $91.6(4)^\circ$ and C-C bond lengths between $1.438(7)$ Å and $1.473(6)$ Å. The asymmetry in the C-C bond lengths coincides with differences in the Zr-C distances ($2.350(5)$ – $2.471(5)$ Å), where longer C-C bonds are associated with shorter Zr-C bonds (Figure 3). Based on ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR data (Figures S9–13), the cyclobutadiene ligand undergoes rapid rotation about the Zr-centroid axis resulting in equivalent phenyl substituents and a single ^{13}C resonance for the cyclobutadiene core at 114.85 ppm in benzene- d_6 . Additionally, the phenyl substituents exhibit free rotation about the C-C bond to the cyclobutadiene moiety. VT-NMR experiments in toluene- d_8 confirmed low barriers for both processes and rapid rotation on the NMR timescale. Having established the identity of the photochemical product, the quantum yield for the formation of $(\text{MePMP}^{\text{Me}})_2\text{Zr}(\eta^4\text{-C}_4\text{Ph}_4)$ was determined as 7%.

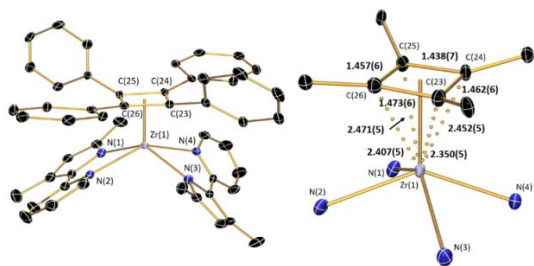


Figure 3. Top: Representation of the molecular structure of $(\text{MePMP}^{\text{Me}})_2\text{Zr}(\eta^4\text{-C}_4\text{Ph}_4)$ with 30% probability ellipsoids. Hydrogen atoms have been omitted for clarity. Bottom: Selected bond distances for the $\text{Zr}(\eta^4\text{-C}_4\text{Ph}_4)$ core.

While η^4 -cyclobutadiene complexes of late transition metals are well known, early transition metal examples are relatively rare.^{25–30} Among group 4 metals, only titanium has been reported to form η^4 -cyclobutadiene complexes.^{31–35} The sole example for a zirconium cyclobutadiene adduct of any kind, prior to this work, was reported by Sharp et al. and features an η^2 -bound benzocyclobutadiene ligand.³⁶ However, structural features and reactivity of the compound resemble those of cyclobutene complexes indicating that the second π -electron pair of the cyclobutadiene moiety contributes primarily to the 6π -electron system of the annulated benzene ring rather than

the π -system of the cyclobutadiene. The isolation of a bona fide zirconium η^4 -cyclobutadiene complex in the course of our study prompted investigations of its electronic structure using DFT. Consistent with the low electronegativity of zirconium, the bonding between the cyclobutadiene ligand and the metal centre in $(\text{MePMP}^{\text{Me}})_2\text{Zr}(\eta^4\text{-C}_4\text{Ph}_4)$ is significantly more polarized than the highly covalent interactions established in late transition metal cyclobutadiene complexes.³⁷ Notably, careful inspection of the calculated molecular orbital manifold and the reduced orbital charges indicate that the complex is best described as a Zr^{IV} species (d^0) with a doubly reduced, 6π -electron aromatic cyclobutadienyl(2-) ligand. This is most clearly reflected in the compositions of the doubly occupied HOMO and HOMO-1 (Figure S34), which exhibit majority contributions from the degenerate, non-bonding set of π -orbitals of the cyclobutadiene fragment and only minor contributions from the Zr d_{xz} and d_{yz} orbitals (14% and 9%, respectively).

Additional DFT calculations were performed to probe the thermodynamic stability of $(\text{MePMP}^{\text{Me}})_2\text{Zr}(\eta^4\text{-C}_4\text{Ph}_4)$ with respect to the alternative zirconacyclopentadiene isomer. To benchmark our computational approach, the stability of the well-characterized zirconocene complex $\text{Cp}_2\text{Zr}(\text{C}_4\text{Ph}_4)$ with respect to its hypothetical isomer $\text{Cp}_2\text{Zr}(\eta^4\text{-C}_4\text{Ph}_4)$ was explored first. Consistent with the observed reactivity under thermal and photochemical conditions, the zirconacyclopentadiene adduct was found to be lower in energy by 14.4 kcal mol⁻¹. In contrast, $(\text{MePMP}^{\text{Me}})_2\text{Zr}(\eta^4\text{-C}_4\text{Ph}_4)$ was found to be more stable than the corresponding metallacycle using the same computational method. Two zirconacyclopentadiene isomers with *trans*-coordinating pyrrole and pyridine moieties were considered and showed higher energies by 6.8 and 8.7 kcal mol⁻¹, respectively. Inspired by these computational results, the synthesis of $(\text{MePMP}^{\text{Me}})_2\text{Zr}(\eta^4\text{-C}_4\text{Ph}_4)$ under thermal conditions was explored. While the thermolysis of $(\text{MePMP}^{\text{Me}})_2\text{ZrBn}_2$ in the presence of excess diphenylacetylene at 120°C in the dark allowed access to the desired product, significantly extended reaction times of several days were required compared to the rapid photolysis reaction. Additionally, the yield of $(\text{MePMP}^{\text{Me}})_2\text{Zr}(\eta^4\text{-C}_4\text{Ph}_4)$ was substantially lowered under thermal conditions due to the formation of unidentified side products further highlighting the advantages of our photochemical approach.

To gain further insight into the mechanism of light-induced Zr-C bond cleavage in $(\text{MePMP}^{\text{Me}})_2\text{ZrBn}_2$, we conducted a photolysis reaction in the presence of excess 4-methylbenzyl bromide, which resulted in rapid, near quantitative formation of $(\text{MePMP}^{\text{Me}})_2\text{ZrBr}_2$ (Figure 1). Characterization of the organic photolysis products by ^1H NMR spectroscopy and GC/MS analysis unambiguously identified a mixture of bibenzyl, 4-methylbibenzyl, and 4,4'-dimethylbibenzyl (Scheme 1). The relative ratio of the three bibenzyl derivatives established by NMR spectroscopy is close to the theoretical value of 1:2:1 expected from the coupling of free benzyl and 4-methylbenzyl radicals. The latter is the product of bromine atom abstraction from 4-methylbenzyl bromide by transient low-valent

zirconium species. Most importantly, the presence of 4-methylbibenzyl as the major organic by-product of the reaction is inconsistent with concerted reductive elimination upon irradiation, which should provide exclusively the homocoupled bibenzyl derivatives. Stepwise Zr-C bond homolysis with formation of Zr^{III} intermediates was also reported by Erker and coworkers.³⁸

The isolation of (MePMPMe)₂ZrBr₂ allowed us to explore another potential synthetic route to (MePMPMe)₂Zr(η⁴-C₄Ph₄) via reduction with potassium graphite (KC₈) in the presence of diphenylacetylene. Surprisingly, these conditions did not yield the desired cyclobutadienyl complex but provided the zirconacyclopentadiene adduct (MePMPMe)₂Zr(C₄Ph₄) as the major product. While the identity of the product was unambiguously established by X-ray crystallography (Figure 4) and correlated NMR spectroscopy (Figure S14 and S15), isolation of sufficient quantities of pure material has been unsuccessful to date. Preliminary experiments indicate that irradiation of (MePMPMe)₂Zr(C₄Ph₄) results in C-C bond formation yielding (MePMPMe)₂Zr(η⁴-C₄Ph₄); however, more detailed studies are necessary and currently underway.

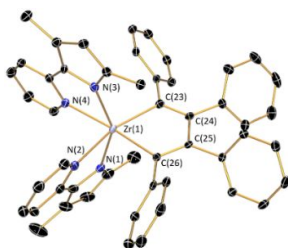


Figure 4. Representation of the molecular structure of (MePMPMe)₂Zr(C₄Ph₄) with 30% probability ellipsoids. Hydrogen atoms have been omitted for clarity.

In conclusion, we report the first example of an η⁴-cyclobutadienyl zirconium complex. The compound can be accessed under mild conditions using visible light photolysis of (MePMPMe)₂ZrBr₂ in the presence of diphenylacetylene. This reactivity is unprecedented for zirconium and stands in stark contrast to the formation of zirconacyclopentadienes usually observed under photochemical and thermal conditions. Our studies suggest that the photochemical activation of organometallic precursors provides a viable pathway for the rapid generation of reactive zirconium intermediates that allow access to unprecedented structural motifs.

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Conflicts of interest

There are no conflicts to declare.

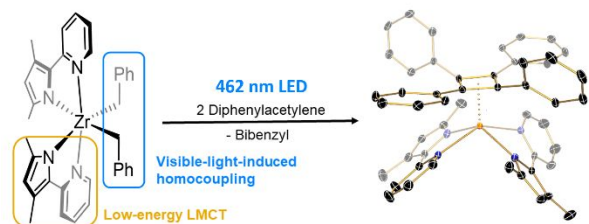
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Table of contents entry



Photochemical activation of an organozirconium precursor in the presence of diphenylacetylene resulted in the isolation and structural characterization of the first zirconium cyclobutadienyl piano stool complex.