

Self-Coupling of a 4-H-Butatrienyldene Tungsten Complex**

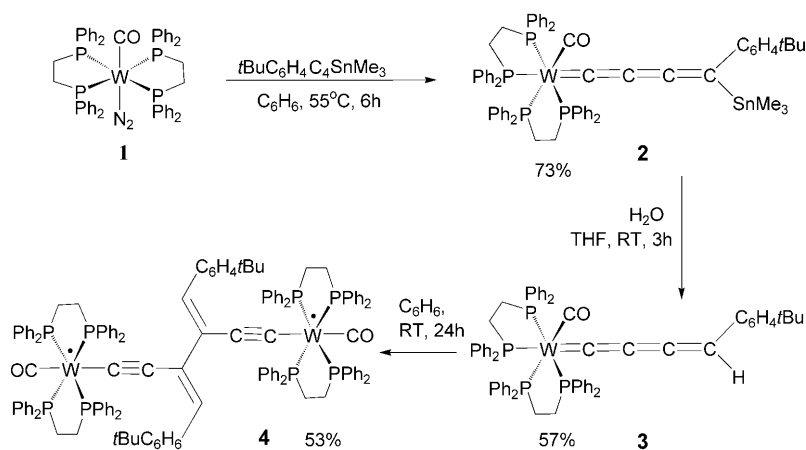
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Organometallic complexes with cumulated π systems as bridges have gained importance in view of potential applications in the emerging field of molecular electronics.^[1] Metallacumulenes by themselves are an interesting class of molecules that have been intensively investigated for their unique structural, reactive, and material properties.^[2] Although metallacumulenes $[L_xM=C(=C)_nRR']$ (R, R' = metal fragment or aromatic groups) with $n \geq 3$ have been isolated and characterized, cumulenes of the type $[L_xM=C(=C)_3HR]$, where R is an organic group, have not been isolated to date.^[3] The terminal R groups apparently have significant influence on the stability of such systems, and this has triggered a search for such stable systems with simple terminal organic functionalities.^[3a] Cumulenes bearing metal derived substituents at their terminal ends remain stable, but often display uncontrolled reactivity that is less suited for the preparation of new materials.^[4] Herein we report the synthesis and characterization of a new stable and terminal secondary butatrienyldene complex of the type $[L_xM=C(=C)_3HR]$.

Organic cumulenes are known to undergo "self-coupling" by a [2+2] addition reaction.^[5] Homocoupling reactions have been observed with metal vinylidene complexes, which have resulted in the formation of dinuclear complexes with π -conjugated bridges that have interesting electronic properties.^[6] However, self-coupling reactions of metal allenylidenes and longer cumulenylidenes remain elusive. One of the reasons for the absence of such coupling reactions can be attributed to the lack of H-substituted cumulenylidenes of the type $[L_xM=C(=C)_nHR]$. Herein, we demonstrate the unprecedented reductive coupling of a butatrienyl complex.

We envisaged that tungsten butatrienyl complexes of the type $[W(CO)(dppe)_2\{C=C=C(SnMe_3)(R)\}]$ could be prepared by the reaction of a 1,3-butadiyne tin derivative with an

electron-rich metal complex $[W(CO)(N_2)(dppe)_2]$ (**1**; dppe = tetraphenyl-1,2-diphosphinoethane) containing a labile N_2 ligand.^[7] Intermediate formation of a but-1-en-3-ynylidene species was expected to be followed by migration of the tin group to the terminal position. To stabilize the cumulenyl complex, the butadiyne $Me_3SnC\equiv CC=C(p-C_6H_4tBu)$ was selected as the acetylenic precursor, as after subsequent deprotection of the ligand, a stable product was expected. Compound **1** indeed reacts with $Me_3SnC\equiv CC=C(p-C_6H_4tBu)$ in an evacuated Young's tube at 55 °C for 6 h (Scheme 1; see the Supporting Information for details).



Scheme 1. Formation of compounds 2–4.

The product $[W(CO)(dppe)_2\{C=C=C(SnMe_3)(p-C_6H_4tBu)\}]$ (**2**) was isolated as red crystals in 73 % yield. The ^{31}P NMR spectrum revealed the *cis* position of the diphosphines, and the ^{13}C NMR spectrum showed four resonances for the C_4 cumulenyl chain at $\delta = 267.6$ ($W=C_o$), 162.6 ($=C_p$), 140.0 ($=C_r$), and 70.7 ppm ($=C_s(SnMe_3)(p-C_6H_4tBu)$). These data are comparable to those obtained for MnC_4 derivatives.^[3a] The $C-Sn$ bond in **2** is very reactive, and removal of $SnMe_3$ was easily achieved with equimolar amounts of water in the form of a 0.01 % THF solution. The deprotected compound $[W(CO)(dppe)_2\{C=C=C=CH(p-C_6H_4tBu)\}]$ (**3**) was fully characterized by NMR and IR spectroscopy and elemental analysis. The presence of the terminal $CH(p-C_6H_4tBu)$ group in **3** was confirmed by ($^1H, ^{13}C$) correlation, ^{13}C -DEPT, and $^1H\{^{31}P\}$ -decoupling NMR experiments. The $CH(p-C_6H_4tBu)$ protons appear at $\delta = 3.74$ ppm as a triplet with $^6J(^1H, ^{31}P) = 4.0$ Hz. The solid-state structures of **2** (see the Supporting Information) and **3** (Figure 1) were confirmed by an X-ray diffraction study.^[8] Both complexes have similar structural parameters. The

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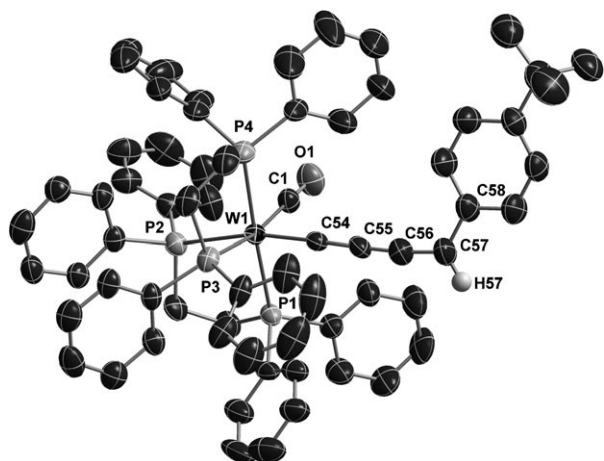
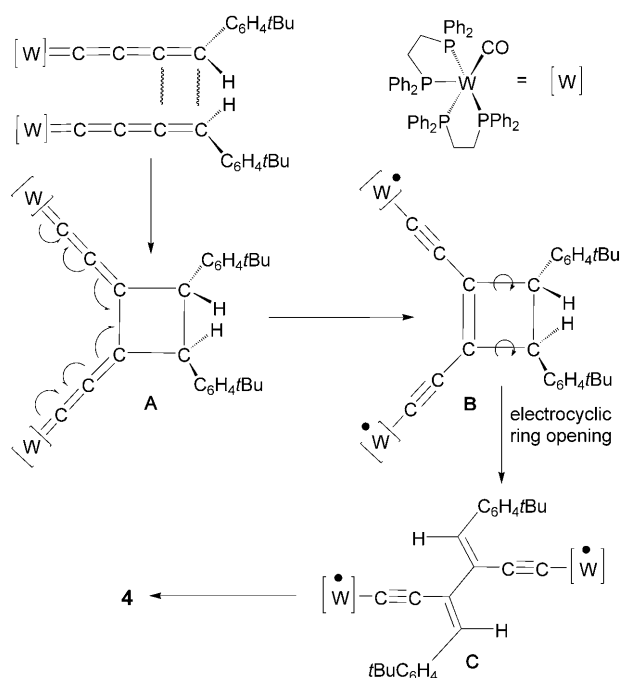


Figure 1. Molecular structure of **3** (ellipsoids set at 50% probability). Apart from H57, hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: W1–C54 1.915(6), C54–C55 1.305(8), C55–C56 1.274(9), C56–C57 1.349(9).

unsaturated carbon chain deviates only slightly from linearity. The C54–C55 and C56–C57 bonds are both longer than the internal C55–C56 bond. This is in contrast to Ir–C₄ and Mn–C₄ cumulenic species.^[3a,9] Prolonged storage of **3** in solution at room temperature resulted in [3,3'-bis(*trans*-(4-*p*-*tert*-butylphenyl)buta-3-en-1-yl)bis(tetraphenyl-1,2-diphosphinoethane)carbonyltungsten] (**4**; Scheme 1), and diffusion of pentane into a benzene solution of **3** gave brown crystals of the coupled molecule in 53% yield. Formation of **4** can be envisaged to occur by coupling at the C3 atom of **3** with subsequent rearrangement of the diphosphine ligands from *cis* to *trans*.^[7] Such a dimerization process has only been observed for organic butatrienes to date,^[10] however, the mechanism pertaining to the organic analogue cannot be applied to the reaction of **3**.

Among many pathways, a [2+2] cycloaddition process with the formation of a cyclobutane intermediate **A** is putatively preferred (Scheme 2), as it has been frequently observed with organic cumulenes and was also detected earlier for metal cumulenes.^[5,11] Thus it could be rationalized that the reaction of **3** proceeds through a [2+2] cycloaddition between the terminal C_v=C_δ double bonds, forming a intermediate **A**. Owing to the electron-accepting ability of the energetically very low-lying LUMO of the bisallenylidene system and the energetically high-lying d orbital of the metal, a two-electron metal-to-ligand redox process takes place. This process presumably occurs with stepwise electron transfers, forming a cyclobutene intermediate **B**, which subsequently opens by an electrocyclic reaction. DFT calculations of the LUMOs of allenylidene, butatrienylidene, and the bisallenylidene ligands revealed energies of –3.26, –2.98, and –4.99 eV, respectively, making clear that the bisallenylidene is the most susceptible system for the internal redox process.^[12] Recently, such internal redox processes leading often to antiferromagnetic ground states have been more frequently observed.^[13] The observed stereochemistry demands formation of mainly the *Z,Z* stereoisomer that originates from the sterically controlled *trans* position of the



Scheme 2. Plausible mechanism for dimerization of **3**.

p-C₆H₄*t*Bu substituent in **A**. This formation is followed by stereoselective conrotatory electrocyclic ring-opening, leading to *E,E* or *Z,Z* stereoisomers of **C**, where *Z,Z* is sterically preferred. This mechanism is consistent with the stability of the tin derivative, in which the bulky SnMe₃ group prevents the initial approach of the double bonds.

The kinetics of the reaction were investigated by probing the concentration dependence of the dimerization reaction of **3**; the concentration was monitored by integration of the C₈H proton signal in the ¹H NMR spectrum (Figure 2). The data

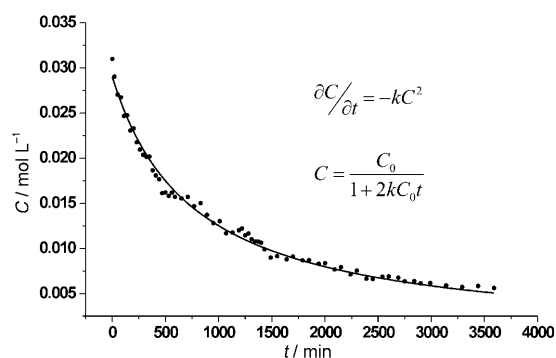


Figure 2. Time dependence of the concentration of **3** in the dimerization process at 25 °C. $C_{\text{start}} = 0.031 \text{ mol L}^{-1}$.

could be fitted with second-order kinetics; the estimated rate constant *k* is 0.0227 L mol^{–1} min^{–1}. The second-order nature of the reaction additionally confirms that the rate-limiting step involves two parent molecules. The calculated value of Δ*U* from DFT calculations for the dimerization process is 22.3 kcal mol^{–1}.

The molecular structure (Figure 3) of **4** revealed an octahedral tungsten center with a squared phosphorus environment and an average W-P distance of 2.475(1) Å and mutually *trans* CO and alkynyl ligands.^[8] The conjugated

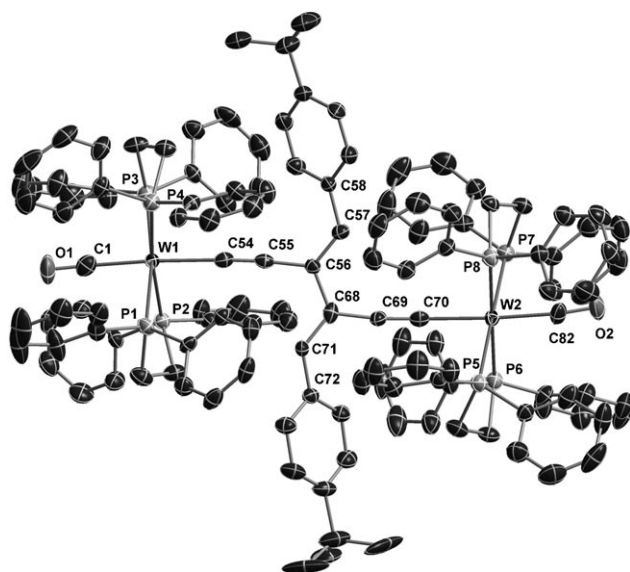


Figure 3. Molecular structure of **4** (ellipsoids set at 50% probability). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: W1–C54 2.160(5), C54–C55 1.215(7), C55–C56 1.459(7), C56–C57 1.340(6), C56–C68 1.495(6), C71–C68 1.374(7), C68–C69 1.444(7), C69–C70 1.233(7), W2–C70 2.176(5). Non-bonding and average distances [Å]: W1–W2 10.323(1), C(sp)≡C(sp) 1.224(7), C(sp²)=C(sp²) 1.357(6), C(sp)–C(sp²) 1.452(6).

part of the molecule is almost planar, with an average deviation of the atoms from the plane (C54–C58/C68–C72/W1/W2) of 0.14(1) Å. Based on the C–C bond lengths, compound **4** indeed possesses an 2,3-ethynyl substituted 1,3-butadiene bridge. The bridge in **4** is very reminiscent of the cross-conjugation of π systems, which is crucial to precisely control electron conduction along two different directions that would enable the creation of two-way molecular electronic switches. Metal centers with a d⁵ low spin configuration as in **4** have interesting electrochemical and magnetic properties.

To probe the redox behavior of the open-shell molecule **4**, cyclic voltammetry studies were carried out, and show two reversible stepwise reductions filling the electronic holes at the tungsten centers (Figure 4). Furthermore, **4** undergoes an irreversible two-electron oxidation. The peak separation $\Delta E = 154$ mV for reversible reduction results in a disproportionation constant $K_c = 400$, which shows that it is a class II compound according to the Robin and Day classification,^[14] which is quite reasonable for a C₆ bridge with a moderately delocalized π system.

The magnetic properties of **4** were established by variable-temperature magnetization measurements and by EPR spectroscopy (Figure 5). The magnetic susceptibility of **4** shows a maximum at 20 K (the Neel temperature), and it

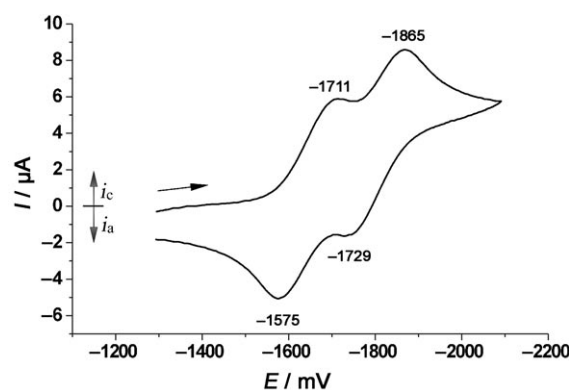


Figure 4. Cyclic voltammogram for **4** in 0.1 M [nBu₄N][PF₆]. Pt electrode, E versus Fc^{0/+}, scan rate = 50 mVs⁻¹, 20 °C.

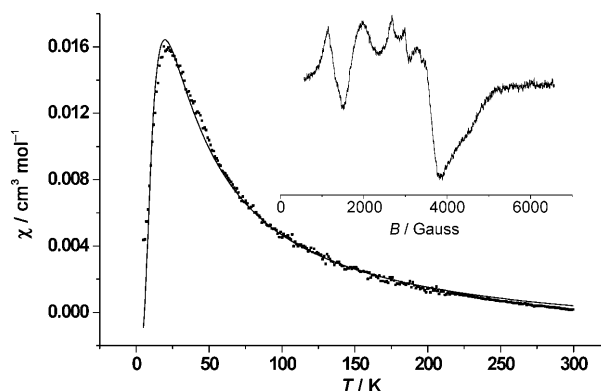


Figure 5. Temperature dependence of the molar magnetic susceptibility χ versus temperature T for **4**. The inset shows the EPR spectrum of solid **4** at 10 K.

drops considerably on going to higher temperatures. Thus, the magnetic behavior of **4** is typical of an antiferromagnetically coupled spin dimer.

To obtain an estimate of the exchange coupling, we fitted the experimental data with equation for a spin- $1/2$ dimer model:

$$\chi = \frac{2N_A g^2 \beta^2}{kT} \cdot \frac{1}{(3 + e^{J/kT})} + \chi_0$$

with g , J , and χ_0 as parameters. The χ_0 accounts for core diamagnetism, van Vleck paramagnetism, and other temperature-independent contributions. The derived J indicates a singlet–triplet gap equal to -21 cm⁻¹, which is similar to that observed for tungsten(V) dinuclear μ -phenolate complexes.^[15] The antiferromagnetic nature of the spin interactions can be explained by the spin-polarization mechanism involving six p orbitals of the bridge.^[16]

A very broad signal centered about $g = 1.9$ was observed in EPR spectra. A more narrow signal at $g = 5.0$ is associated with transition having $\Delta m_s = 2$ (simultaneous flipping of two electron spins). A similar kind of behavior has been observed for compounds with two tungsten(V) centers.^[15]

In conclusion, we have shown for the first time that a 4-H metal butatrienylidene, such as $[\text{W}(\text{CO})(\text{dppe})_2\{\text{C}=\text{C}=\text{C}=\text{C}(\text{H})(\text{R})\}]$, becomes stable when it has an aromatic organic terminal functionality. Under controlled reaction conditions, it was serendipitously found that this molecule undergoes an unusual coupling at the 3-position of the carbon chain to form a novel diethynyl butadiene bridged dimer **4** with interesting electrochemical and magnetic properties. The unique combination of a cross-conjugated π system and paramagnetic centers makes this type of molecule a unique model for the investigation of the Kondo effect on the molecular level.^[17] The carbon framework in this transformation involves a complex sequence and comprises the three-step conversion of the butadiyne into the final diethynyl butadiene via a butatrienylidene species. We believe that this work opens interesting avenues in the field of organometallic cumulene chemistry and molecular electronics.

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