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

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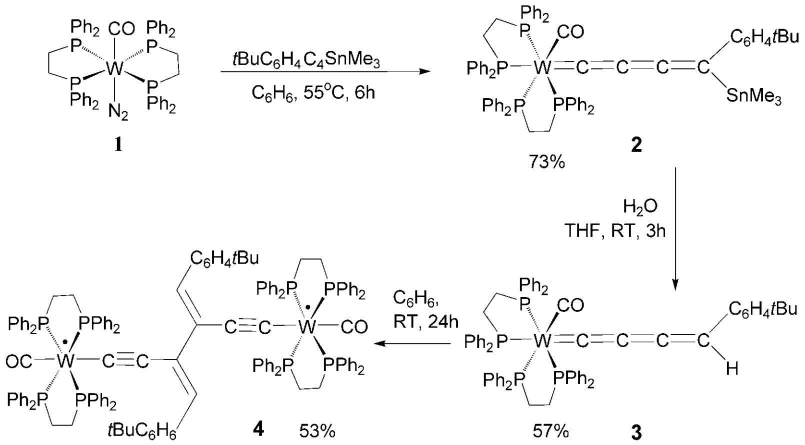
Organometallic complexes with cumulated π systems as bridges have gained importance in view of potential applications in the emerging field of molecular electronics.[1] Metallacumulenes by themselves are an interesting class of molecules that have been intensively investigated for their unique structural, 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 butatrienylidene 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 $[W(CO)(dppe)_2\{C{=}C{=}C{=}C(SnMe_3)(R)\}]$ 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 cumulenic complex, the butadiyne $Me_3SnC{\equiv}CC{\equiv}C(p\text{-}C_6H_4tBu)$ was selected as the acetylenic precursor, as after subsequent deprotection of the ligand, a stable product was expected. Compound **1** indeed reacts with $Me_3SnC{\equiv}CC{\equiv}C(p\text{-}C_6H_4tBu)$ 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 $[W(CO)(dppe)_2\{C{=}C{=}C{=}C(SnMe_3)(p\text{-}C_6H_4tBu)\}]$ (**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 cumulenic chain at $\delta = 267.6$ ($W{=}C_\alpha$), 162.6 ($={C_\beta}=$), 140.0 ($={C_\gamma}=$), and 70.7 ppm ($={C_\delta}(SnMe_3)(p\text{-}C_6H_4tBu)$). 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 $[W(CO)(dppe)_2\{C{=}C{=}C{=}CH(p\text{-}C_6H_4tBu)\}]$ (**3**) was fully characterized by NMR and IR spectroscopy and elemental analysis. The presence of the terminal $CH(p\text{-}C_6H_4tBu)$ group in **3** was confirmed by (^1H,^{13}C) correlation, ^{13}C-DEPT, and $^1H\{^{31}P\}$-decoupling NMR experiments. The $CH(p\text{-}C_6H_4tBu)$ 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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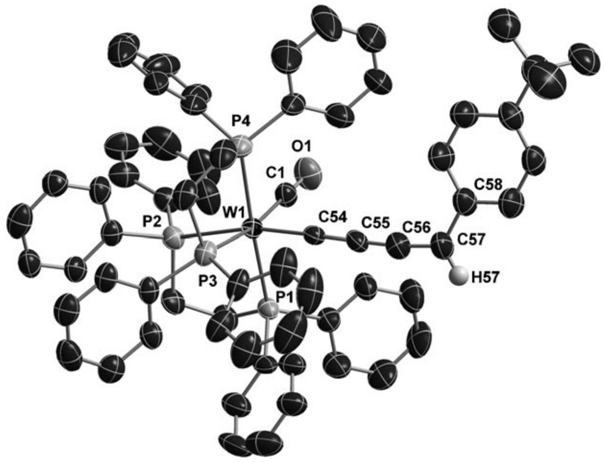
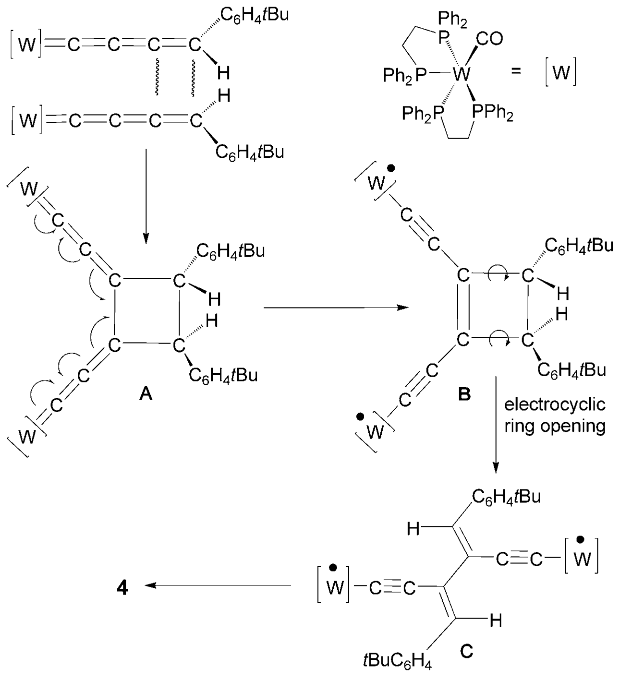


Figure 1. Molecular structure of **3** (ellipsoids set at 50% probability). Apart from H57, hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: W1–C54 1.915(6), C54–C55 1.305(8), C55–C56 1.274(9), C56–C57 1.349(9).



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

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-C$_4$ and Mn-C$_4$ cumulenic species.[3a,9] Prolonged storage of **3** in solution at room temperature resulted in [3,3′-bis{*trans*-(4-*p*-*tert*-butylphenylbuta-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 $C_\gamma = C_\delta$ 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 *p*-C$_6$H$_4$*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 SnMe$_3$ 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 $C_\delta H$ proton signal in the ^{1}H NMR spectrum (Figure 2). The data 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 ΔU from DFT calculations for the dimerization process is 22.3 kcal mol^{-1}.

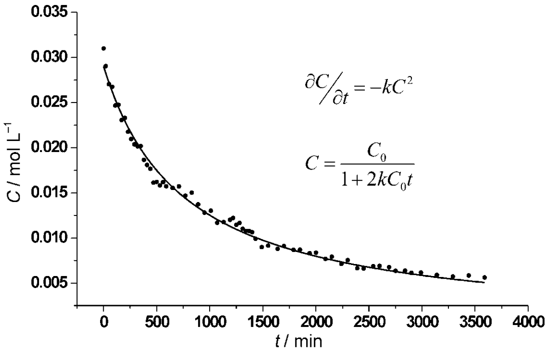


Figure 2. Time dependence of the concentration of **3** in the dimerization process at 25 °C. $C_{\text{start}} = 0.031$ mol L^{-1}.

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 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 d^5 low spin configuration as in **4** have interesting electrochemical and magnetic properties.

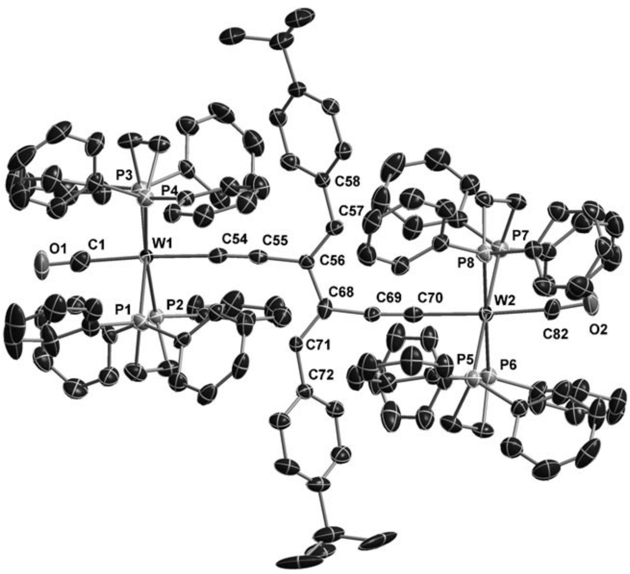


Figure 3. Molecular structure of **4** (ellipsoids set at 50% probability). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: W1–C54 2.160(5), C54–C55 1.215(7), C55–C56 1.459(7), C56–C57 1.340(6), C56–C68 1.495(6), C71–C68 1.374 (7), C68–C69 1.444(7), C69–C70 1.233(7), W2– C70 2.176(5). Non-bonding and average distances [Å]: W1–W2 10.323(1), C(sp)≡C(sp) 1.224(7), C(sp^2)=C(sp^2) 1.357(6), C(sp)–C(sp^2) 1.452(6).

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 comproportionation 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 C_6 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 drops considerably on going to higher temperatures. Thus, the magnetic behavior of **4** is typical of an antiferromagnetically coupled spin dimer.

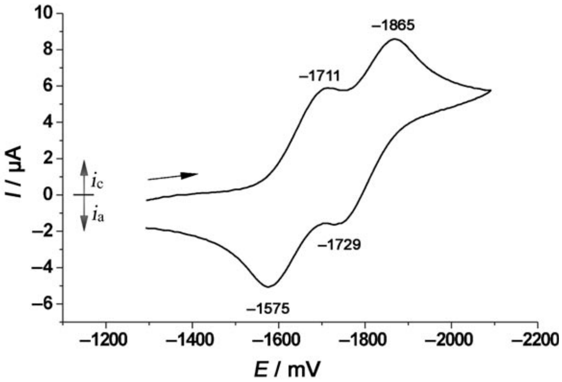


Figure 4. Cyclic voltammogram for **4** in 0.1 M [nBu_4N][PF_6]. Pt electrode, E versus $Fc^{0/+}$, scan rate = 50 mVs^{-1}, 20 °C.

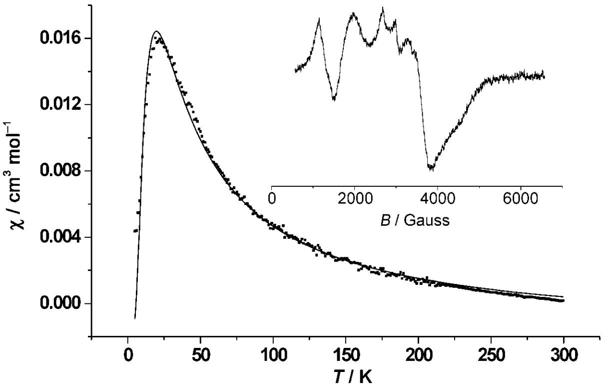


Figure 5. Temperature dependence of the molar magnetic susceptibility χ versus temperature T for **4**. The inset shows the EPR spectrum of solid **4** at 10 K.

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 $-21\ \text{cm}^{-1}$, 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 $[\mathrm{W(CO)(dppe)_2\{C{=}C{=}C{=}C(H)(R)\}}]$, 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 butatreienylidene species. We believe that this work opens interesting avenues in the field of organometallic cumulene chemistry and molecular electronics.

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