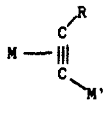
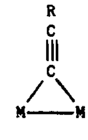
(2.2–2.3 Å).[15] The very acute C1–C2–W angle of 97.3 (8)° indicates that there is some bonding interaction between W and C1 despite the long W–C1 distance (2.53 (1) Å); otherwise, this angle would open up to about 120° to minimize contacts between ancillary ligands on tungsten and ruthenium.

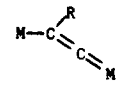
Bridging alkynyls are capable of a broad range of bonding modes, typically adopting either μ_2-η^1:η^2 (A)[16] or *sym*-μ_2-η^1:η^1 (B)[17] arrangements. No bona fide example of a μ_2-η^1:$\eta^{1'}$-alkynyl (metal-substituted vinylidene, C) has been reported, although $[\{Fe(CO)_2(\eta\text{-}C_5Me_5)\}_2(\mu_2\text{-}\eta^1\text{:}\eta^2\text{-}C{\equiv}CR)]BF_4$ (R = H and Ph)[17a] show distortions toward C.[18–20] The solid-state structure of **3a** even more closely resembles a cationic ruthenium complex bearing a tungsten-substituted vinylidene ligand (C), with nearly complete loss of the π-bond of A. The best description of **3a** is probably D, which can alternatively be considered as a carbenium ion center at C_α stabilized by three-center, two-electron bonding to the two metals.



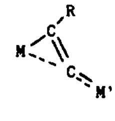
A



B



C



D

We are pursuing two-electron oxidations of ethynediyls **4a–e** to μ-bicarbide dications $[W{=}C{=}C{=}M]^{2+}$. A cyclic voltammogram of **4e** in THF shows a reversible one-electron oxidation at 0.36 V and a second irreversible oxidation at 0.91 V, but attempts to carry out the oxidation on a preparative scale have been unsuccessful.

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Supplementary Material Available: Preparative and spectroscopic details for compounds **3a–e** and **4a–e** and listings of crystal structure data, positional and thermal parameters, bond distances and angles, torsion angles, and least-squares planes for **3a** (19 pages); experimental and calculated structure factors for **3a** (26 pages). Ordering information is given on any current masthead page.

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(18) The distances from Fe to the α and β carbon atoms are 2.422 (5) and 2.114 (6) Å for μ-C≡CH, and 2.357 (5) and 2.134 (6) Å for μ-C≡CPh.[17a] The bridging phenylethynyl ligands in $[(Cp)(CO)_3W(\mu\text{-}\eta^1\text{:}\eta^2\text{-}C{\equiv}CPh)W(CO)(PhC{\equiv}CH)(Cp)][BF_4]$[19] and $[Zr_2(\mu\text{-}C{\equiv}CPh)_2(MeC_5H_4)_4]$[20] also show slight distortions toward C.

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Carbanion Photochemistry: A New Photochemical Route to Strained Cyclic Allenes

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Photoexcitation of allyl anions results in increased charge density at C2.[1] As a consequence, substitution at this position by an efficient leaving group should provide a route to allenes or related isomers. We have previously found that 2-chloro-1,3-diphenylindenyl anion undergoes photoelimination to produce an intermediate characterized as 1,3-diphenylisoindenylidene.[2] We describe here a photochemical route to 1-phenyl- and 1,3-diphenyl-1,2-cyclohexadiene.[3] Confirmation of an allene intermediate is provided in one case by preparation through a conventional carbenoid route.

1-Chloro-2-phenylcyclohexene and 1-chloro-2-phenylcyclopentene were prepared by reaction of the 2-phenylcycloalkanone with PCl_5 in benzene and purified by fractional distillation. 1-Chloro-2,6-diphenylcyclohexene was prepared by reaction of 2,6-diphenylcyclohexanone[4] under similar conditions. Treatment with potassium *tert*-butoxide in Me_2SO produced efficient deprotonation, as was indicated by the rapid formation of red-brown to purple solutions of the anions. Furan was added, and the solutions were irradiated with light from a 450-W Hanovia lamp filtered through 0.1 M $K_2Cr_2O_7$ ($\lambda > 450$ nm) to avoid irradiation of the parent chlorocarbons. Products were isolated by washing with water, ether extraction, and chromatography over alumina. The six-membered-ring anion (**1a**) yielded a trace of biphenyl plus a single major product, mp 92–93 °C (50% yield), characterized as an endo adduct of furan and 1-phenyl-1,2-cyclohexadiene.[5] Single-crystal X-ray diffractometry showed the adduct to have structure **3a**.[6] A similar reaction in the presence of diphenyl-

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(5) The spectral data were as follows: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.16–7.35 (5 H, m), 6.46 (1 H, dd, J = 1.76, 5.64), 6.29 (1 H, dd, J = 1.66, 5.62), 5.84 (1 H, dd, J = 2.76, 4.58), 5.16 (1 H, s), 5.01 (1 H, d, J = 1.26), 2.19 (1 H, dt, J = 3.44, 11.68), 2.06 (1 H, dd, J = 8.38, 18.90), 1.92–1.99 (1 H, m), 1.46–1.53 (1 H, m), 1.11–1.23 (1 H, m), 0.76–0.84 (1 H, m); MS (70 eV) 224 (M^+, 33.2), 196 (25.4), 195 (100), 181 (18.6), 167 (32.2), 115 (18.6), 91 (25.1), 77 (11.5). Anal. C, H.

(6) Crystallographic data of **3a** [$C_{11}H_{16}O$ (fw 224.0)] are as follows: monoclinic space group $P2/c$; a = 20.082 (6) Å, b = 6.524 (2) Å, c = 9.092 (2) = Å; β = 96.15 (2)°; V = 1184.4 (6) Å^3; D_{calcd} = 1.26 g/cm^3 (Z = 4). A total of 2082 independent reflections were collected on a Syntex $P2_1$ diffractometer using graphite-monochromated Mo Kα radiation. The final R factor was 0.074 for 1406 reflections with $F_o > 3\sigma(F_o)$.

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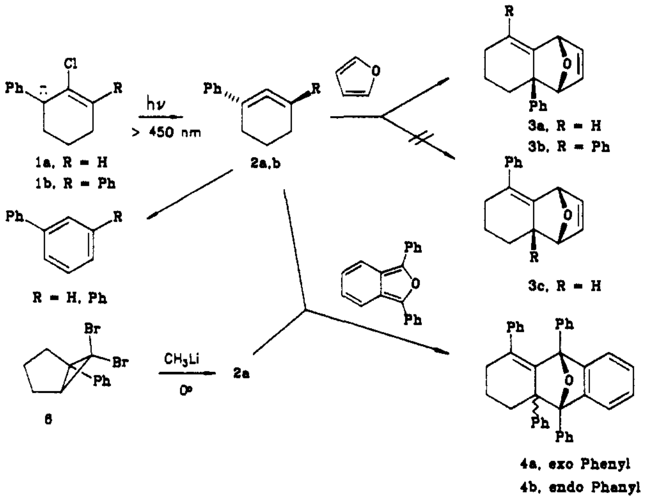
isobenzofuran afforded adducts **4a** and **4b** in a 4:1 ratio.[7] 1,3-Diphenyl-1,2-cyclohexadiene was also generated and trapped by furan to yield adduct **3b**, mp 124-125 °C, in similar fashion.[8]

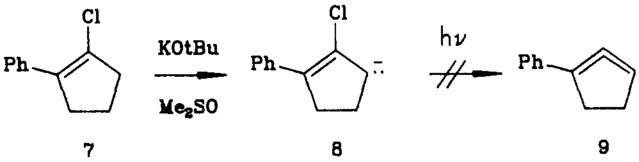


Confirmation of intermediate allene **2a** was obtained by a second route. Dibromocarbene addition to 1-phenylcyclopentene afforded thermally unstable adduct **6** in 20% yield. Treatment of **6** with CH_3Li in the presence of diphenylisobenzofuran gave adducts **4a** and **4b** in the same ratio as from **1a** photolysis. This route to 1,2-cyclohexadienes is well precedented[3] and confirms the intermediacy of **2a** from anion photolysis. Attempted reaction of **6** with CH_3Li in the presence of furan gave only products of furan lithiation.

Thermolysis of anion **1a** or **1b** and furan in THF at 50 °C for 20 h gave the same cycloadducts **3a** and **3b** in good yield. In the absence of furan, biphenyl became the major product from photolysis or thermolysis of anion **1a**, while *m*-terphenyl was formed from **1b**. One logical mechanism includes base-catalyzed rearrangement of the allene to a 1,3-cyclohexadiene, which aromatizes upon workup.

The cycloadditions of allene **2a** are regiospecific and display high stereoselectivity, despite the high reactivity and expectation of a highly nonsynchronous mechanism.[9] Initial bonding at the central allene carbon relieves ca. 30 kcal/mol of strain;[10] this is followed by closure at the sites of higher odd electron density. AM1 calculations on **2a** predict a chiral allenic structure, with a C1-C2-C3 angle of 134°. Frontier MO coefficients are greater at the styryl centers, which also is consistent with the observed regiospecificity.

Surprisingly, there was no evidence that irradiation of **8** provided 1-phenyl-1,2-cyclopentadiene (**9**); precursor **7** was recovered unchanged, along with a minor amount of dehalogenation product 1-phenylcyclopentene. It is possible that the anion does not undergo elimination because of the increased strain in **9**, or anion **8** may undergo a spontaneously *reversible* electron ejection[1] or electrocyclic opening.



Photodehalogenation of chlorocarbanions continues to provide an excellent route to novel reactive intermediates. The ready formation and efficient cycloaddition of 1,2-cyclohexadienes suggest more general applications in synthesis as well as routes to other reactive intermediates.

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(7) Adducts **4a** and **4b** were isolated by preparative TLC. Data include the following. **4a**: ^1H NMR ($CDCl_3$, 360 MHz) δ 7.84-7.86 (2 H, br d, 7.10 Hz), 7.74-7.75 (2 H, br d, 7.19 Hz), 7.56-7.60 (2 H, br t, 7.48 Hz), 7.47-7.51 (2 H, br t, 7.88 Hz), 7.35-7.45 (5 H, m), 7.05-7.12 (3 H, m), 6.83-6.90 (3 H, m), 1.84-1.98 (2 H, m), 1.36-1.61 (3 H, m), 1.17-1.31 (1 H, m); ^{13}C NMR ($CDCl_3$) δ 148.76, 146.38, 144.71, 141.22, 137.48, 136.43, 129.16, 128.48, 127.95, 127.45, 127.34, 126.92, 126.61, 126.35, 126.26, 125.92, 125.85, 120.73, 119.57, 119.07, 91.92, 89.81, 56.16, 30.36, 21.15, 17.49. Anal. C, H. **4b**: ^1H NMR δ 7.99-8.02 (2 H, m), 7.48-7.59 (4 H, m), 7.42-7.44 (m, 2 H), 7.12-7.31 (6 H, m), 6.92-6.98 (m, 5 H), 5.93-5.95 (1 H, dd, 4.67, 2.94 Hz), 2.64-2.69 (1 H, td, 11.64, 3.42 Hz), 1.81-1.99 (2 H, m), 1.46-1.55 (1 H, m), 1.21-1.32 (1 H; m), 0.91-0.99 (1 H, dt, 11.98, 4.16); ^{13}C NMR δ 150.0, 147.6, 145.1, 142.1, 137.9, 135.1, 129.6, 128.7, 128.6, 128.4, 127.8, 127.3, 126.9, 126.7, 125.6, 125.5, 125.3, 123.3, 121.9, 117.4, 93.6, 89.2, 56.9, 32.1, 24.1, 18.7. Anal. C, H.

(8) Adduct **3c** is assigned the exo stereochemistry by analogy with **3a** and by its similar spectral properties: ^1H NMR ($CDCl_3$, 300 MHz) δ 7.19-7.44 (10 H, m), 6.37 (2 H, m), 5.40 (1 H, br s), 5.06 (1 H, br s), 2.28-2.35 (3 H, m), 1.63-1.66 (1 H, m), 1.29-1.36 (1 H, m), 0.92-1.01 (1 H, m); MS (70 eV) 300 (M^+, 69.2), 271 (100.0), 228 (61.0), 215 (33.0), 202 (35.1), 165 (55.0), 128 (31.0), 115 (68.1), 91 (88.0), 77 (39.3). Anal. C, H.

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Geminal Selectivity of Singlet Oxygen Ene Reactions. The Nonbonding Large Group Effect

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The mechanism of the ene reaction of singlet oxygen with olefins has received extensive experimental and theoretical attention over the last several years.[1] Although recent theoretical calculations[2] support an earlier proposed concerted mechanism,[3] it is generally accepted that the ene reaction proceeds through an intermediate.[1] The regioselective addition of singlet oxygen to alkenes has received less attention. In the last few years it has been shown that $^1O_2$ adds to trisubstituted alkenes with syn selectivity[4] and to unsymmetrical *cis*-alkenes with regioselective double-bond formation in the larger group.[5]

Recently geminal selectivity has been found to favor the alkyl group on the double-bond carbon that bears an electron-withdrawing group in either a vinylic or allylic relationship, as shown in Scheme I.

To date, these results have been rationalized by invoking (a) the formation of trioxenes[6a,7] and [4 + 2] adducts;[11] (b) polar

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