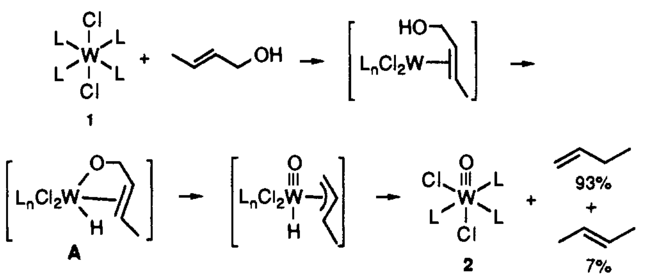
Scheme II



Thiols are desulfurized by **1** to form alkanes and the tungsten sulfido complex **3**, without any evidence for the formation of thiolate complexes (eq 2; R = Et, ^{t}Bu). These reactions are much

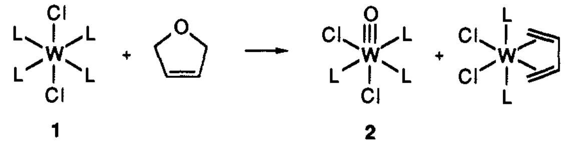
$$\underset{\mathbf{1}}{WCl_2(PMePh_2)_4} + RSH \rightarrow \underset{\mathbf{3}}{W(S)Cl_2(PMePh_2)_3} + RH + PMePh_2 \quad (2)$$

more rapid than those with alcohols: ethanethiol is desulfurized in 10 min at ambient temperatures and ^{t}BuSH within an hour, while deoxygenation of ethanol requires 3 weeks and ^{t}BuOH is unreactive. The reaction of **1** and ^{t}BuSH initially forms **3** and isobutane in high yields,[9] but **3** reacts further with the thiol to give a complex mixture of products including $SPMePh_2$. With EtSH, degradation of **3** by the thiol is competitive with its formation and **3** does not accumulate in the reaction mixture. Aryl thiols yield hydrogen[8] and apparently paramagnetic products which have not been characterized.

In contrast to the slow reactions of **1** with saturated alcohols, allyl alcohol is very rapidly (<1 min) and quantitatively[9] converted to **2** and propene (Scheme I).[13] Similarly, allyl mercaptan is desulfurized within 1 min. 3-Buten-1-ol is also rapidly deoxygenated, to 1-butene, indicating that conjugation is not responsible for the faster rates of unsaturated substrates. Rates are affected by steric hindrance about the double bond (Scheme I), with the trisubstituted olefin reacting as slowly as aliphatic alcohols. The rate enhancement thus seems to result from coordination of the double bond to the tungsten center, consistent with the rapid formation of a bis(ethylene) complex from **1** and ethylene.[5a] Double-bond migration is observed on deoxygenation of 3-buten-2-ol and 2-buten-1-ol, both isomers yielding 93:7 mixtures of 1-butene and *trans*-2-butene (by NMR).

The deoxygenation does not appear to proceed via free-radical intermediates, as no ethane is observed on methanol reduction, nor butane or ethylene from EtOH, and CH_3OH is reduced to CH_4 even in toluene-d_8. The reaction of benzyl alcohol with **1** is similar to that of methanol, both in rate and in the ratio of products. In C_6D_6 solution, CD_3OD is reduced to CD_4 and allyl alcohol-*O-d* forms $CH_2{=}CHCH_2D$. Carbocations also seem unlikely as aromatic alkylation and ether formation are not observed.[14] The observation of the same nonthermodynamic product mixture from isomeric butenols (Scheme I) suggests a common intermediate, probably an η^3 or fluxional 1-methylallyl complex. These data are consistent with a mechanism for the deoxygenation of allyl alcohols (Scheme II) involving initial coordination of the double bond, followed by oxidative addition of the O–H bond[15] to form an allyloxy intermediate (A). The rate enhancement for unsaturated alcohols is then due to oxidative addition being an intramolecular process. Intermediate A can rearrange[16] to an oxo–allyl–hydride species[17] which reductively eliminates alkene. An alternative involving loss of RH directly from A[18] is difficult to reconcile with the observed double-bond migration.

This chemistry has been extended to ethers by using the idea that the double bond acts as a tether to bring the oxygen to the metal center. Thus 2,5-dihydrofuran and diallyl ether are rapidly deoxygenated to give **2** (e.g., eq 3[19]), while THF and Et_2O do not react with **1** at ambient temperatures.



(3)

Deoxygenation of alcohols and ethers (net oxygen atom transfer) is a quite unusual reaction. The formation of the very strong tungsten–oxygen multiple bond in **2**[20] provides a driving force for this pathway as opposed to the more common reduction of alcohols to alkoxide compounds. Further studies of the mechanism and the scope of these unusual transformations are in progress, including the differences between alcohols, thiols, and amines (which are not reduced to imido complexes[21]).

Acknowledgment. We thank Dr. Jeff Bryan for discovering reaction 3 and for his insightful advice. This work was supported by the National Science Foundation and the Chevron Research Co.

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(13) With excess allyl alcohol, $W(O)Cl_2(CH_2{=}CHCH_2OH)(PMePh_2)_2$ is formed in equilibrium with **2** and can be the predominant product.[6b] Similar equilibria are observed for the other terminal alkenols as well. All of the unsaturated alcohol reactions appear to proceed in high yield.[9]

(14) Cf.: Noble, A. M.; Winfield, J. M. *J. Chem. Soc. A* **1970**, 501–506.

(15) Cf.: Reference 11. Wilkinson, G.; Chiu, K. W.; Jones, R. A.; Galas, A. M. R.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* **1981**, 1204. Oxidative addition of the C–O bond instead of the C–H bond is also possible, followed by loss of alkene from a W(OH)(allyl) species; cf.: Herrmann, W. A.; Kuchler, J. G.; Weichselbaumer, G.; Herdtweck, E.; Kiprof, P. *J. Organomet. Chem.* **1989**, *372*, 351–370.

(16) Parkin, G.; Bunel, E.; Burger, B. J.; Trimmer, M. S.; Van Asselt, A.; Bercaw, J. E. *J. Mol. Catal.* **1987**, *41*, 21–39.

(17) Oxo-allyl complexes: Spaltenstein, E.; Erikson, T. K. G.; Critchlow, S. C.; Mayer, J. M. *J. Am. Chem. Soc.* **1989**, *111*, 617–623. Atagi, L. A.; Mayer, J. M., unpublished results.

(18) Listemann, M. L.; Schrock, R. R.; Dewan, J. C.; Kolodziej, R. M. *Inorg. Chem.* **1988**, *27*, 264–271.

(19) Bryan, J. C. Ph.D. Thesis, University of Washington, 1988. Reaction with dihydrofuran proceeds in high yield[9] to a roughly 3:1 mixture of **2** and $WCl_2(C_4H_6)(PMePh_2)_2$.

(20) D(W≡O) is estimated to be >138 kcal/mol.[6d]

(21) Over, D.; Mayer, J. M., unpublished results.

Ruthenium–Tungsten and Iron–Tungsten Complexes with Ethynyl and Ethynediyl Bridges

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Small carbon fragments are important in the surface chemistry of many heterogeneous catalysts,[1] often as reactive intermediates[2] or as precursors to graphitic overlayers.[1] While metal cluster carbides are relatively common,[3] complexes with carbide[4] and

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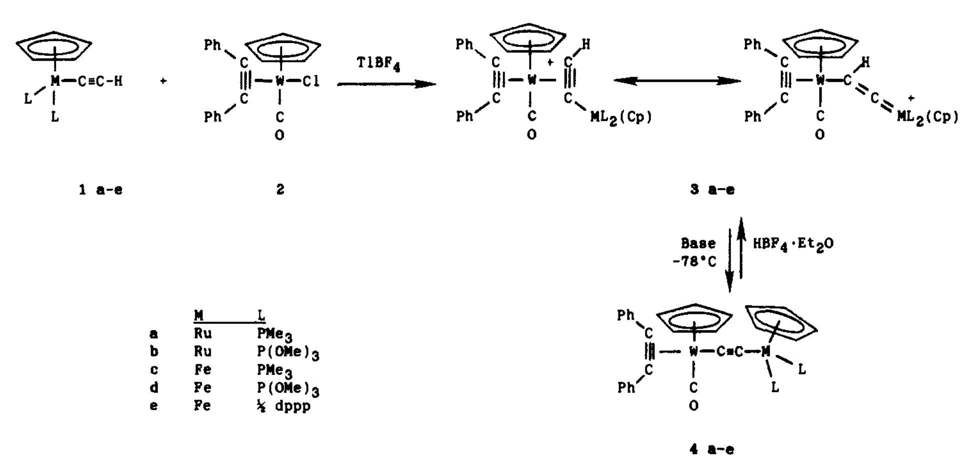
(1) (a) Somorjai, G. A. *Chemistry in Two Dimensions: Surfaces*; Cornell University Press: Ithaca, NY, 1981; pp 494–499. (b) Viswanathan, B. *J. Mol. Catal.* **1986**, *37*, 157–163. (c) Bianchi, D.; Tau, L. M.; Borcar, S.; Bennett, C. O. *J. Catal.* **1983**, *84*, 358–374. (d) Erdöhelyi, A.; Solymosi, F. *J. Catal.* **1983**, *84*, 446–460. (e) Erly, W.; McBreen, P. H.; Ibach, H. *J. Catal.* **1983**, *84*, 229–234. (f) Orita, H.; Naito, S.; Tamaru, K. *J. Catal.* **1988**, *111*, 464–467. (g) Stockwell, D. M.; Bianchi, D.; Bennett, C. O. *J. Catal.* **1988**, *113*, 13–25. (h) Shincho, E.; Egawa, C.; Naito, S.; Tanaru, K. *Surf. Sci.* **1985**, *155*, 153. (i) Duncan, T. M.; Winslow, P.; Bell, A. T. *J. Catal.* **1985**, *93*, 1.

(2) (a) Anderson, R. B. *The Fischer-Tropsch Synthesis*; Academic Press: 1984. (b) Chisholm, M. H.; Folting, K.; Hampden-Smith, M. J.; Hammond, C. E. *J. Am. Chem. Soc.* **1989**, *111*, 7283–7285.

(3) (a) Johnson, B. F. G.; Lewis, J.; Nelson, W. J. H.; Nicholls, J. N.; Vargas, M. D. *J. Organomet. Chem.* **1983**, *249*, 255–272. (b) Bradley, J. S. *Adv. Organomet. Chem.* **1983**, *22*, 1. (c) Tachikawa, M.; Muetterties, E. L. *Prog. Inorg. Chem.* **1981**, *28*, 203. (d) Hriljac, J. A.; Swepston, P. N.; Shriver, D. F. *Organometallics* **1985**, *4*, 158–166. (e) Chisholm, M. H. *J. Organomet. Chem.* **1987**, *334*, 77–84.

0002-7863/90/1512-6414$02.50/0

Scheme I



	M	L
a	Ru	PMe3
b	Ru	P(OMe)3
c	Fe	PMe3
d	Fe	P(OMe)3
e	Fe	½ dppp

bicarbide[5] ligands bridging just two or three metals are quite rare. We present here several heterometallic complexes with bridging ethynyl (—C≡CH) and ethynediyl (—C≡C—) ligands, as possible models for low-coordinate surface carbides.

Reactions of iron and ruthenium ethynyls [M(C≡CH)L_2(Cp)] (**1a–e**, Scheme I)[6] with [WCl(CO)(PhC≡CPh)(Cp)][7] in the presence of $TlBF_4$ lead to ethynyl-bridged complexes [(Cp)L_2M(μ-C≡CH)W(PhC≡CPh)(CO)(Cp)][BF_4] (**3a–e**). For the iron phosphine complexes, vinylidenes [Fe(C=CH_2)L_2(Cp)]$^+$ are formed as byproducts along with **3c** and **3e**, probably by protonation of unreacted **1c** and **1e** by acidic **3c** and **3e**. Spectroscopic data, especially ethynyl ^{1}H NMR shifts (δ 10.19, 11.20, 8.90, 10.90, and 11.20 for **3a–e**, respectively), suggested that the ethynyl bridges were η^2-bonded to tungsten and η^1-bonded to ruthenium in complexes **3a–e**.[8,9] Deprotonation of phosphine μ-ethynyls **3a**, **3c**, and **3e** using NaN(SiMe_3)$_2$ or of phosphite μ-ethynyls **3b** and **3d** using KOCMe_3 gave ethynediyl-bridged complexes [(Cp)L_2M(μ-C≡C)W(PhC≡CPh)(CO)(Cp)] (**4a–e**, Scheme I). Complexes with ethynediyl bridges between transition metals are quite rare,[10] and complexes **4** are the first with two different transition metals. Reprotonation of [(Cp)(PMe_3)$_2$Ru(μ-C≡C)W(PhC≡CPh)(CO)(Cp)] (**4a**) using HBF_4·Et_2O regenerated **3a**.

The X-ray crystal structure of [(Cp)(PMe_3)$_2$Ru(μ-C≡CH)W(PhC≡CPh)(CO)(Cp)][BF_4][11] (Figure 1) revealed a geometry

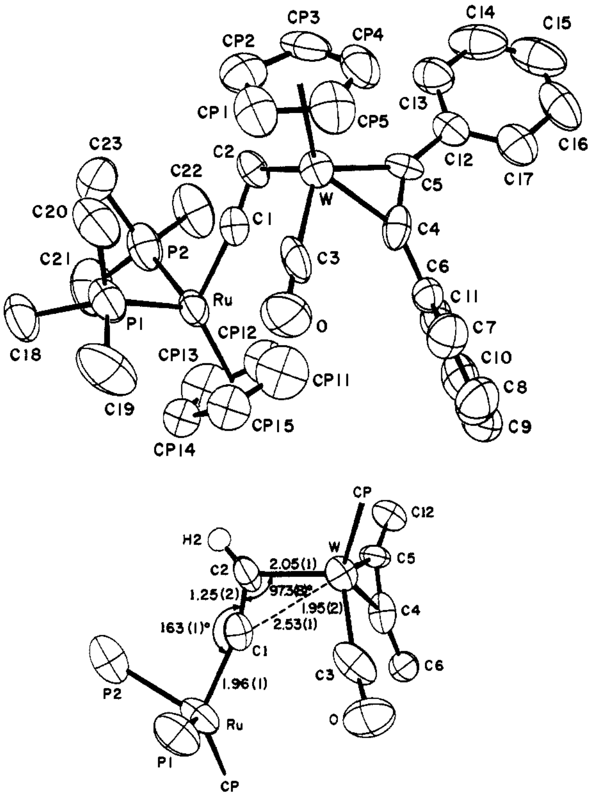


Figure 1. ORTEP[23] plots of the structure of **3a** showing 50% probability ellipsoids, with selected bond distances (Å) and angles. H2 is placed in a calculated position.

in which the ethynyl bridge is σ-bonded to ruthenium but distinctly distorted from η^2 geometry at tungsten, contrary to solution spectroscopic data. The Ru–C1 bond (1.96 (1) Å) is slightly shorter than in ruthenium alkynyls (2.00–2.02 Å), but longer than in cationic ruthenium vinylidene and CO complexes (1.82–1.87 Å).[12] The Ru–C1–C2 angle (163 (1)°) remains nearly linear. The W–C2 bond length (2.05 (1) Å) falls in the normal range for tungsten η^2-alkynes[9] and η^2-ketenyls (2.0–2.1 Å),[13] but is significantly shorter than in most tungsten alkyls[14] or an η^1-ketenyl

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(4) (a) Latesky, S. L.; Selegue, J. P. *J. Am. Chem. Soc.* **1987**, *109*, 4731–4733. (b) Goedken, V. L.; Deakin, M. R.; Bottomley, L. A. *J. Chem. Soc., Chem. Commun.* **1982**, 607–608. (c) Mansuy, D.; Lecomte, J.-P.; Chottard, J.-C.; Bartoli, J.-F. *Inorg. Chem.* **1981**, *20*, 3119–3121. (d) Ercolani, C.; Gardini, M.; Goedken, V. L.; Pennesi, G.; Rossi, G.; Russo, U.; Zanonato, P. *Inorg. Chem.* **1989**, *28*, 3097–3099. (e) Guilard, R.; Kadish, K. M. *Chem. Rev.* **1988**, *88*, 1121–1146.

(5) (a) Neithamer, D. R.; LaPointe, R. E.; Wheeler, R. A.; Richeson, D. S.; Van Duyne, G. D.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1989**, *111*, 9056–9072. (b) Blau, R. J.; Chisholm, M. H.; Folting, K.; Wang, R. J. *J. Am. Chem. Soc.* **1987**, *109*, 4552–4560. (c) Listemann, M. L.; Schrock, R. R. *Organometallics* **1985**, *4*, 74–83.

(6) Ethynyl complexes **1a–e** were prepared by the deprotonation of [M(C_2H_2)(PR_3)$_2$(Cp)]$^+$ using KOCMe_3, following the method previously reported for the preparation of **1a**: Bullock, M. *J. Chem. Soc., Chem. Commun.* **1989**, 165.

(7) Davidson, J. L.; Green, F.; Stone, F. G. A.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1976**, 738.

(8) Compare [M(HC≡CR)$_2$(CO)(Cp)]$^+$ (M = Mo, W): Templeton, J. L. *Adv. Organomet. Chem.* **1989**, *29*, 1–100.

(9) Kolobova, N. E.; Skripkin, V. V.; Rozantseva, T. V.; Struchkov, Y. T.; Aleksandrov, G. G.; Antonovich, V. A.; Bakhmutov, V. I. *Sov. J. Coord. Chem.* (*Engl. Transl.*) **1982**, *8*, 1655–1663.

(10) (a) Pt, Pd: Ogawa, H.; Onitsuka, K.; Joh, T.; Takahashi, S.; Yamamoto, Y.; Yamazaki, H. *Organometallics* **1988**, *7*, 2257–2260. (b) Re: Appel, M.; Heidrich, J.; Beck, W. *Chem. Ber.* **1987**, *120*, 1087–1089. (c) Re: Beck, W.; Niemer, B.; Breimair, J.; Heidrich, L. *J. Organomet. Chem.* **1989**, *372*, 79–83. (d) Re: Heidrich, J.; Steimann, M.; Appel, M.; Beck, W.; Phillips, J. R.; Trogler, W. C. *Organometallics* **1990**, *9*, 1296. (e) Au: Nast, R.; Schneller, P.; Hengefeld, A. *J. Organomet. Chem.* **1981**, *214*, 273–276. (f) Au: Cross, R. J.; Davidson, M. F.; McLennan, A. J. *J. Organomet. Chem.* **1984**, *265*, C37–C39. (g) V: Kreisel, G.; Scholz, P.; Seidel, W. *Z. Anorg. Allg. Chem.* **1980**, *460*, 51–55. (h) Ru_4: Bruce, M. I.; Snow, M. R.; Tiekink, E. R. T.; Williams, M. L. *J. Chem. Soc., Chem. Commun.* **1986**, 701.

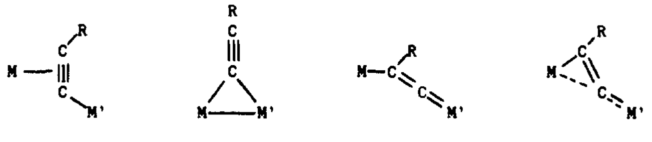
(11) Crystal data for **3a**: CAD4 diffractometer, Mo Kα radiation, 5928 reflections, 4075 with $(F_o)^2 \geqslant 3\sigma(F_o)^2$ for refinement, $P2_1/c$, $Z = 4$, a = 11.305 (2) Å, b = 13.443 (6) Å, c = 23.283 (7) Å, β = 103.27 (2)°, V = 3443.94 Å^3, ρ_{calcd} = 1.726 g·cm^{-3}, μ = 39.74 cm^{-1}, empirical absorption correction (CAMEL[21]), solved using direct methods and DIRDIF,[22] 1:1 disordered Cp on Ru, H atoms idealized, nongroup atoms refined with anisotropic thermal parameters to R = 5.6%, R_w = 6.4%.

(12) (a) Wisner, J. M.; Bartczak, T. J.; Ibers, J. A. *Inorg. Chim. Acta* **1985**, *100*, 115. (b) Bruce, M. I.; Humphrey, M. G.; Snow, M. R.; Tiekink, E. R. T. *J. Organomet. Chem.* **1986**, *314*, 213–225.

(13) Birdwhistell, K. R.; Tonker, T. L.; Templeton, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 4474–4483.

(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.



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.

Acknowledgment. We are grateful to the U.S. Department of Energy (DE-FG05-85ER13432), the Kentucky EPSCoR program (NSF Grant RII-8610671), and the Ashland Oil Foundation for financial support, to the University of Kentucky Major Research Instrumentation Bond Program for equipment, and to Johnson-Matthey, Inc., for a loan of ruthenium trichloride.

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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(14) Kirtley, S. W. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 3, Chapter 28.1, pp 1255–1319.

(15) Kreissl, F. R.; Uedelhoven, W.; Eberl, K. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 859.

(16) Reviews: (a) Carty, A. J. *Pure Appl. Chem.* **1982**, *54*, 113–130. (b) Nast, R. *Coord. Chem. Rev.* **1982**, *47*, 89–124. (c) Holton, J.; Pearce, R.; Yarrow, P. I. W.; Lappert, M. *Chem. Rev.* **1983**, *83*, 135–201.

(17) Representative μ-C≡CH complexes: (a) Akita, M.; Terada, M.; Oyama, S.; Moro-oka, Y. *Organometallics* **1990**, *9*, 816. (b) Fritz, P. M.; Polborn, K.; Steimann, M.; Beck, W. *Chem. Ber.* **1989**, *122*, 889. (c) Beck, W. *Polyhedron* **1988**, *7*, 2255–2261. (d) Cowie, M.; Loeb, S. J. *Organometallics* **1985**, *4*, 852–857.

(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 $[(Cp)(CO)_3W(\mu\text{-}\eta^1\text{:}\eta^2\text{-}C{\equiv}CPh)W\text{-}(CO)(PhC{\equiv}CH)(Cp)][BF_4]$[19] and $[Zr_2(\mu\text{-}C{\equiv}CPh)_2(MeC_5H_4)_4]$[20] also show slight distortions toward C.

(19) Kolobova, N. E.; Skripkin, V. V.; Rozantseva, T. V.; Struchkov, Y. T.; Aleksandrov, G. G.; Andrianov, V. G. *J. Organomet. Chem.* **1981**, *218*, 351–359.

(20) (a) Erker, G.; Frömberg, W.; Benn, R.; Mynott, R.; Angermund, K.; Krüger, C. *Organometallics* **1989**, *8*, 911–920. (b) Kumar, P. N. V.; Jemmis, E. D. *J. Am. Chem. Soc.* **1988**, *110*, 125–131.

(21) (a) Flack, H. D. *Acta Crystallogr.* **1974**, *30A*, 569–573. (b) Flack, H. D. *Acta Crystallogr.* **1977**, *33A*, 890–898. (c) Flack, H. D.; Vincent, M. G. *Acta Crystallogr.* **1978**, *34A*, 489–491.

(22) (a) Beurskens, P. T.; Bosman, W. P.; Doesburg, H. J.; Gould, R. O.; van den Hark, T. E. M.; Prick, P. A. J.; Noordik, J. H.; Beurskens, G.; Parthasarthi, V.; Bruins Slot, H. J.; Haltiwanger, R. C.; Strumpel, M.; Smits, J. M. M. *DIRDIF*; Crystallography Laboratory, Toernooiveld, Technical Report 1984/1, 6525 ED Nijmegen, Netherlands, 1984. (b) Buerskens, P. T.; Prick, P. A. J.; van den Hark, T. E. M.; Gould, R. O. *Acta Crystallogr.* **1980**, *36A*, 653–656.

(23) Johnson, C. K. Report ORNL 5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

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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(1) For a general review of carbanion photochemistry, see: (a) Tolbert, L. M. *Acc. Chem. Res.* **1986**, *19*, 268. (b) Tolbert, L. M. The Excited States of Resonance-Stabilized Anions. In *Comprehensive Carbanion Chemistry, Part C*; Buncel, E., Ed.; Elsevier: New York, 1987; pp 223–270.

(2) (a) Tolbert, L. M.; Siddiqui, S. *J. Am. Chem. Soc.* **1984**, *106*, 5538. (b) Tolbert, L. M.; Siddiqui, S. *Ibid.* **1982**, *104*, 4273.

(3) For reviews of strained allenes, see: Johnson, R. P. *Chem. Rev.* **1989**, *89*, 1111.

(4) Brown, R. F. C.; Hadman, G. J.; Leppick, R. A. *Aust. J. Chem.* **1972**, *25*, 2049.

(5) The spectral data were as follows: ^1H 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; $\beta = 96.15$ (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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