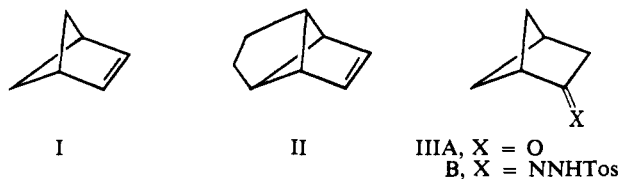


The Synthesis of Bicyclo[2.1.1]hex-2-ene¹

Sir:

Whereas the chemistry of bicyclo[2.1.1]hexanes has been explored to a considerable extent during the last decade,² the corresponding parent olefin, bicyclo[2.1.1]hex-2-ene (I), has never been described. Much to our surprise, even the Hofmann elimination sequence re-



cently reported for the synthesis of the closely related tricyclo[3.3.0.0^{2,6}]oct-2-ene (II)³ was unsuccessful when applied to the simpler bicyclic nucleus.⁴ We now report the successful application of a newly described olefin synthesis to this problem.^{5,6}

The readily accessible bicyclo[2.1.1]hexan-2-one (IIIA)⁷ was converted into its *p*-toluenesulfonylhydrazone (IIIB)⁸ which, in a typical experiment, was treated with excess ethereal methyllithium at room temperature for 15 hr. After quenching the reaction mixture with water, most of the ether was removed by careful distillation. The residue, which contained two main hydrocarbon products, was subjected to preparative gas chromatography. The component of shorter retention time, formed in about 25% yield from IIIB, was established to be the desired I on the basis of the following evidence. (1) Its mass spectrum shows a parent peak at *m/e* 80 (C₆H₈⁺) and a base peak at 79 (C₆H₇⁺). (2) Its nmr spectrum (60 Mc, external TMS) shows olefinic absorption centered at τ 3.38 (2 H) and saturated proton absorptions centered at τ 7.66 (4 H) and 7.91 (2 H). (3) Catalytic hydrogenation in absolute ethanol over Adams catalyst resulted in the uptake of 1 equiv of hydrogen. The isolated product was indistinguishable from an authentic sample of bicyclo[2.1.1]hexane on the basis of glpc comparison on two columns, as well as by nmr and mass spectral comparisons.

Since I is the only olefin which could give rise to bicyclo[2.1.1]hexane on catalytic reduction, the success of the toluenesulfonylhydrazone-alkyllithium technique in this case is established, and it would appear that this method will be especially useful for the synthesis of highly strained olefins.^{9,10}

(1) The partial support of this research by a National Science Foundation grant and by the Chevron Research Co. is acknowledged with pleasure.

(2) For a recent review of this area, see J. Meinwald and Y. C. Meinwald, *Advan. Alicyclic Chem.*, **1**, 1 (1966).

(3) The synthesis of a tricyclic analog of I, tricyclo[3.3.0.0^{2,6}]oct-3-ene, was reported by J. Meinwald and B. E. Kaplan, *J. Am. Chem. Soc.*, **89**, 2611 (1967).

(4) Unpublished results with R. A. Chapman, and also private communication from Professor F. T. Bond.

(5) R. H. Shapiro and M. J. Heath, Abstracts of Papers of the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, S104; R. H. Shapiro and M. J. Heath, *J. Am. Chem. Soc.*, **89**, 5734 (1967).

(6) G. Kaufman, F. Cook, H. Schechter, J. Bayless, and L. Friedman, *ibid.*, **89**, 5736 (1967).

(7) F. T. Bond, H. L. Jones, and L. Scerbo, *Tetrahedron Letters*, 4685 (1965).

(8) Satisfactory elemental analytical data were obtained for this compound.

(9) Aside from unsuccessful approaches to I via Hofmann elimination, amine oxide pyrolysis, acetate pyrolysis, and xanthate pyrolysis of a

The ultraviolet absorption spectrum of I is most unusual for a simple, disubstituted ethylene. In *n*-pentane solution maximal absorption appears at 220 m μ ($\epsilon \sim 1300$), with a shoulder at 226 m μ ($\epsilon \sim 1000$). In the gas phase vibrational fine structure shows maxima at 204.4, 205.2, 207.1, 207.9, 208.7, 210.8, 211.5, and 215.2 m μ . These spectral data bear a striking resemblance to those observed for II.³ Further work with both olefins is now being undertaken.

variety of bicyclo[2.1.1]hexanes were all unrewarding in earlier studies in this laboratory.

(10) The second hydrocarbon product, of longer glpc retention time, isolated from the reaction of IIIB with methyllithium is tentatively characterized as 2-methylbicyclo[2.1.1]hexane on the basis of spectral evidence.

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Preparation and Configuration of

4,6,8-Trimethylazulenetetra-ruthenium Enneacarbonyl.

A Complex with Azulene Coordinated to Three Metal Atoms¹

Sir:

Recent crystallographic studies on the azulene-metal carbonyl complexes C₁₀H₈Fe₂(CO)₅,² C₁₀H₈Mo₂(CO)₆,^{3,4} (*i*-C₃H₇)(CH₃)₂C₁₀H₅Mo₂(CO)₆,³ [C₁₀H₈-Mo(CO)₃CH₃]₂,⁵ and C₁₀H₈Mn₂(CO)₆⁶ have revealed a variety of azulene-metal bonding schemes. Continuing the systematization of azulene-metal carbonyl chemistry, we have investigated the reaction of 4,6,8-trimethylazulene⁷ with Ru₃(CO)₁₂ and now report the isolation and characterization of a complex in which azulene is bonded to three atoms of a tetrahedral metal cluster.

Ru₃(CO)₁₂ (0.48 g) and 4,6,8-trimethylazulene (0.58 g) in ligroin (bp 90-120°, 25 ml) were heated under reflux for 96 hr. After removal of solvent under vacuum and reactants by sublimation, the resulting dry material was dissolved in 60:40 ethylene dichloride-cyclohexane and chromatographed on Florisil. Mass spectral analysis of the two products indicated them to be Ru₆(CO)₁₇C⁸ and (CH₃)₃C₁₀H₅Ru₄(CO)₉ (in order of elution).

The azulene-ruthenium carbonyl species appears to crystallize in two modifications, monoclinic and triclinic.⁹ Monoclinic crystals of diamagnetic, air-stable (CH₃)₃C₁₀H₅Ru₄(CO)₉ are obtained as small red parallelepipeds crystallizing in the spacegroup P2₁/n with *a* =

(1) Work supported by the National Science Foundation and the Advanced Research Projects Agency.

(2) M. R. Churchill, *Chem. Commun.*, 450 (1966); *Inorg. Chem.*, **6**, 190 (1967).

(3) M. R. Churchill and P. H. Bird, *Chem. Commun.*, 746 (1967).

(4) J. S. McKechnie and I. C. Paul, *ibid.*, 747 (1967).

(5) P. H. Bird and M. R. Churchill, *ibid.*, 705 (1967); *Inorg. Chem.*, **7**, 349 (1968).

(6) P. H. Bird and M. R. Churchill, *Chem. Commun.*, in press.

(7) This substituted azulene was used in order to avoid such disorder problems as are found in C₁₀H₈Mo₂(CO)₆^{3,4} and in azulene itself.

(8) B. F. G. Johnson, R. D. Johnston, and J. Lewis, *Chem. Commun.*, 1057 (1967).

(9) Single-crystal diffraction studies on the triclinic modification are currently in progress and will be reported at a later date.

$8.99 \pm 0.02 \text{ \AA}$, $b = 18.56 \pm 0.03 \text{ \AA}$, $c = 14.44 \pm 0.02 \text{ \AA}$, $\beta = 96.5 \pm 0.1^\circ$, $V = 2394 \text{ \AA}^3$, $Z = 4$. Observed and calculated densities are 2.29 ± 0.02 and 2.279 g cm^{-3} , respectively. A complete set of X-ray diffraction data ($\sin \theta_{\max} = 0.38$) was collected on a 0.01° incrementing Buerger automated diffractometer. The structure was solved by conventional Patterson, Fourier, and least-squares refinement techniques, the present discrepancy index being $R_F = 0.095$ for 1844 independent, nonzero reflections. Estimated standard deviations are $\sim 0.004 \text{ \AA}$ for metal-metal, $\sim 0.025 \text{ \AA}$ for metal-carbon, and $\sim 0.04 \text{ \AA}$ for carbon-carbon bond lengths.

The molecule possesses approximate C_s symmetry (Figure 1a), with the four ruthenium atoms defining a distorted tetrahedron in which interatomic distances range from 2.70 to 2.90 \AA (Figure 1b). The 4,6,8-trimethylazulene ligand is arched across the largest face of the tetrahedral ruthenium cluster and is bent across C(9)–C(10), C(8)···C(4), and C(7)···C(5) to such an extent that there is a dihedral angle of 113° between the planar five-membered ring and the plane defined by C(5), C(6), and C(7). The three ruthenium atoms associated with the azulene (*i.e.*, Ru(1), Ru(2), Ru(3)) are each bonded to *two* terminal carbonyl ligands, whereas the apical Ru(4) is linked to *three* terminal carbonyl groups.

All important azulene–ruthenium distances are shown in Table I. [It should be emphasized that ruthenium–

Table I

Atoms	\AA	Atoms	A
(i) Ruthenium–Azulene Distances $< 3.3 \text{ \AA}$			
Ru(1)–C(2)	2.18		
Ru(1)–C(1)	2.22	Ru(1)–C(3)	2.23
Ru(1)–C(9)	2.36	Ru(1)–C(10)	2.33
Ru(3)–C(9)	2.59	Ru(2)–C(10)	2.61
Ru(3)–C(8)	2.27	Ru(2)–C(4)	2.25
Ru(3)–C(7)	2.16	Ru(2)–C(5)	2.18
Ru(3)–C(6)	2.48	Ru(2)–C(6)	2.39
(ii) Carbon–Carbon Distances within Azulene Ligand			
C(1)–C(2)	1.45	C(10)–C(4)	1.61
C(2)–C(3)	1.47	C(4)–C(5)	1.31
C(3)–C(10)	1.40	C(5)–C(6)	1.43
C(10)–C(9)	1.54	C(6)–C(7)	1.52
C(9)–C(1)	1.40	C(7)–C(8)	1.31
		C(8)–C(9)	1.46

methyl distances (Ru(2)···C(11) = 3.42 \AA , Ru(2)···C(12) = 3.46 \AA , Ru(3)···C(12) = 3.48 \AA , Ru(3)···C(13) = 3.40 \AA) are all beyond bonding range, thus negating the possibility of hydride abstraction from a methyl group.] The wide range of Ru–C (azulene) and Ru–Ru distances makes it apparent that the bonding in the present molecule is considerably less easily defined than that in previously studied azulene–metal carbonyl complexes^{2–6} and suggests that the molecule is probably better considered within the framework of a relatively sophisticated molecular-orbital treatment. To a first approximation, however, the structure may be described (and an inert-gas configuration reached for each ruthenium atom) by invoking a bonding system which includes two-electron, three-center bonds. The key to this simplified *rationale* lies in the disposition of p_z orbitals (on atoms C(10), C(9), C(6))

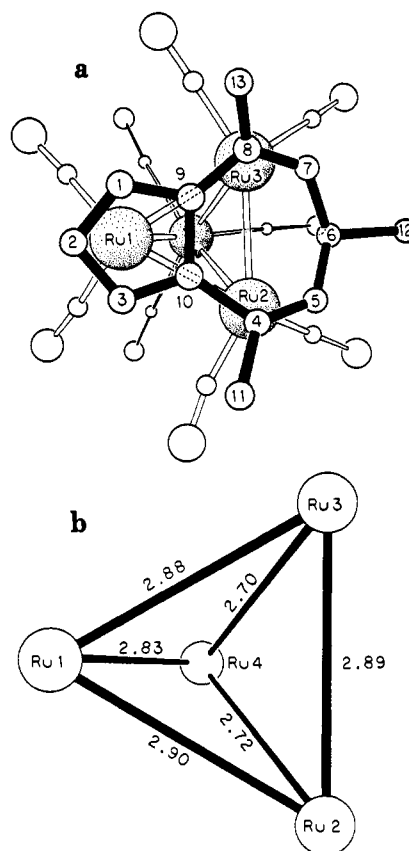


Figure 1. (a) The molecule projected onto the C(8)–C(9)–C(10)–C(4) plane. (b) Interatomic distances within the tetrahedral ruthenium cluster.

which point directly toward the midpoints of metal–metal vectors (see Figure 1a), suggesting two-electron, three-center bonds over Ru(1)–C(10)–Ru(2), Ru(1)–C(9)–Ru(3), and Ru(2)–C(6)–Ru(3).

Using the above scheme, the bonding of Ru(1) to the azulene ligand may be described formally in terms of a π -allyl system (C(1), C(2), C(3)) and two three-center bonds. [It should be realized, however, that the asymmetry of the Ru(1)–C(10)–Ru(2) and Ru(1)–C(9)–Ru(3) bonds is such that the five-membered ring is probably little perturbed from a regular π -cyclopentadienyl system]. Ru(2) and Ru(3) are each linked to the azulene *via* an olefinic bond (to C(4)–C(5), C(7)–C(8), respectively) and two three-center bonds. All carbon–carbon bond lengths within the azulene nucleus are compatible with this proposal (see Table I). Ru(4) is not directly bonded to the azulene ligand and is linked to the other three metal atoms *via* simple σ bonds.

The molecule 4,6,8-trimethylazulene-tetra-ruthenium enneacarbonyl thus joins a small class of compounds ($C_8H_8Fe_2(CO)_5$,¹⁰ $(\pi-C_5H_5)_4Rh_3H$,¹¹ and, possibly, $(C_6H_6)_2Pd_2(Al_2Cl_7)_2$ ¹²) in which an aromatic (or quasi-aromatic) organic residue appears to be bonded to the metal cluster, *per se*, rather than to individual metal atoms.

(10) E. B. Fleischer, A. L. Stone, R. B. K. Dewar, J. D. Wright, C. E. Keller, and R. Pettit, *J. Am. Chem. Soc.*, **88**, 3158 (1966).

(11) E. O. Fischer, O. S. Mills, E. F. Paulus, and H. Wawersik, *Chem. Commun.*, 643 (1967).

(12) G. Allegra, A. Immirzi, and L. Porri, *J. Am. Chem. Soc.*, **87**, 1394 (1965).

It is probable that the " $(C_{10}H_8)_2Fe_3(CO)_{13}$ "¹³ of Burton, *et al.*,¹⁴ will provide a further example of this ligand-to-cluster bonding. A single-crystal structural analysis of this iron complex is currently in progress and will be reported in due course.

(13) Preliminary mass spectral studies show the parent ion peak to be at m/e 760. The accidental mass relationship $^{56}Fe = 2(^{12}C^{16}O)$ leaves us unable to distinguish, at present, between $(C_{10}H_8)_2Fe_3(CO)_8$ or $(C_{10}H_8)_2Fe_4(CO)_{10}$ as the correct formulation.

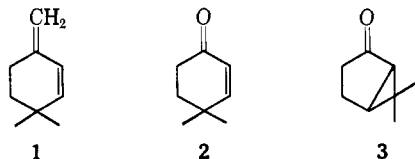
(14) R. Burton, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 4290 (1960).

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The Photochemistry of 4,4-Dimethyl-1-methylene-2-cyclohexene, a Methylene Analog of a Cyclohexenone¹

Sir:

Earlier studies of the photochemical transformation of the transoid dienes of the 1-methylene-2-cycloalkene series have shown that the compounds under singlet conditions (direct irradiation) are readily transformed to their valence isomeric bicyclo[1.1.0]butanes or compounds derivable from such intermediates.² These studies have now been extended to **1**, the methylene analog of 4,4-dimethyl-2-cyclohexenone (**2**), a compound known to undergo the so-called "lumirearrangement" to 6,6-dimethylbicyclo[3.1.0]hexan-2-one (**3**) upon photoexcitation.³ Such a study will permit evaluation of the behavior of a similar compound lacking the $n \rightarrow \pi^*$ excited state.



Reaction of the ketone **2** with methylenetriphenylphosphorane gave 4,4-dimethyl-1-methylene-2-cyclohexene as a colorless liquid:⁴ bp 131–133°; λ_{EtOH}^{max} 232 μ m (ϵ 13,400); $\gamma_{max}^{CCl_4}$ 3030, 2990, 1640, 1600, 1470, 1460, 1360, 880 cm^{-1} ; nmr (τ , CCl_4) AB quartet centered at 4.34 (2 H, $-CH=CH-$, $\delta_A - \delta_B = 0.33$ ppm, $J_{AB} = 9$ cps), 5.32 br singlet (2H, $=CH_2$), triplet centered at 7.67 (2 H, ring CH_2 , $J_{AB} = 7$ cps), triplet centered at 8.52 (2 H, ring CH_2 , $J_{AB} = 7$ cps), singlet 9.01 (6 H, geminal CH_3).

Since the enones are known to undergo the lumirearrangement *via* a triplet,⁵ the triplet of the diene analog **1** was generated. When the irradiation was carried out using triphenylene ($E_T = 68$ kcal) as a sensitizer (Pyrex filter, $\lambda > 280$ μ m) in pentane, starting material was observed to disappear slowly but no monomeric photoproducts were obtained. When the sensitized irradiation

(1) This work was supported in part by PHS Grant 00709, National Institute of Arthritis and Metabolic Diseases, U. S. Public Health Service.

(2) W. G. Dauben and C. D. Poulter, *Tetrahedron Letters*, 3021 (1967).

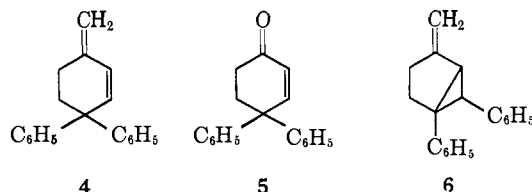
(3) O. L. Chapman, T. A. Rettig, A. A. Griswold, A. I. Dutton, and P. Fitton, *ibid.*, 2049 (1963).

(4) All compounds described gave satisfactory analyses.

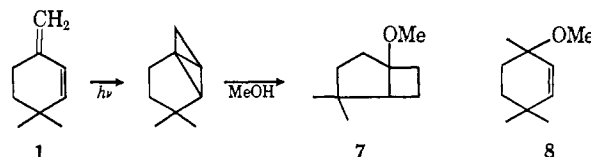
(5) H. E. Zimmerman, R. G. Lewis, J. J. McCullough, A. Padwa, S. W. Staley, and M. Semmelhack, *J. Am. Chem. Soc.*, **88**, 159, 1965 (1966); O. L. Chapman, J. B. Sieja, and W. J. Welstead, Jr., *ibid.*, **88**, 161 (1966).

was repeated using methanol as the solvent, again no monomeric photoproducts and no ethers were formed.⁶ Thus, unlike the enone **2** which is transformed to the lumiproduct **3** *via* the triplet, the triplet of the diene analog **1** behaves as triplets of other exocyclic olefins and slowly polymerizes.⁷ Furthermore, in contrast to the *transoid* dienes such as 3,5-hexalin⁸ and 3,5-cholestadiene⁹ whose internal rotations are constrained and which readily add methanol under sensitized conditions, the unconstrained diene **1**, which is capable of forming an orthogonal triplet, fails to react with methanol.

Recently, Zimmerman and co-workers¹⁰ have investigated the photochemistry of the methylene analog **4** of 4,4-diphenylcyclohexenone (**5**), and it was found that



the diene upon reaction under triplet conditions did not yield any monomeric photoproducts. However, under singlet conditions the *cis* and *trans* isomers of 5,6-diphenyl-2-methylenebicyclo[3.1.0]hexane (**6**) were formed, products which are similar in structure to the photoproducts derived from the triplet of the related enone **5**. Similar studies in this laboratory confirm these results with **4**. When the diene **1** was irradiated directly in pentane, no monomeric rearrangement products were observed. When methanol was used as a solvent, the only monomeric products obtained were the ethers **7** and **8**. Such ethers are typical reaction products formed from a *transoid* diene upon direct irradiation,² **7** coming *via* the bicyclobutane.



Thus, unlike the diphenyl-substituted methylene analog **4**, the dimethyl diene **1** behaves in a manner typical of a normal *transoid* diene in both direct and sensitized irradiation. The formation of a bicyclo[3.1.0]hexane resulting from the rearrangement of a peripheral grouping at position 4 is limited to the 4-phenyl substituent. The inability to form a methylene analog of the typical "lumi" product **3** may be attributed either to the necessity of a $n \rightarrow \pi^*$ triplet in the reaction manifold or to a difference in the charge distribution in a $\pi \rightarrow \pi^*$ triplet of an enone and a diene.

(6) Under conditions where the diene absorbed no light (Pyrex filter), the rate of its disappearance was 20 times that of the sensitizer. Thus, energy transfer from sensitizer to diene occurred.

(7) P. J. Kropp and H. J. Kraus, *J. Am. Chem. Soc.*, **89**, 5199 (1967).

(8) W. G. Dauben and W. T. Wipke, *Pure Appl. Chem.*, **9**, 539 (1964).

(9) J. Pusset and R. Beugelmans, *Tetrahedron Letters*, 3259 (1967).

(10) H. E. Zimmerman and G. E. Samuelson, *J. Am. Chem. Soc.*, **89**, 5971 (1967).

(11) National Institutes of Health Predoctoral Fellow.

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