(ϵ 50)). Compound **7** yielded ketone **10** (mp 95–97°) which was shown to be a cyclohexanone by ir (ν^{CCl_4} 1735 cm^{-1}) and exhibited a red-shifted and intensified n,π^* transition indicating homoconjugation with the aromatic system [$\lambda_{max}^{cyclohexane}$ 298 (ϵ 425), 309 (ϵ 535), 320 (ϵ 470), and 332 nm (ϵ 200)].[10] Compound **8** yielded ketone **11** (mp 137–139°) which was shown to be a cyclopentanone by ir (ν^{CCl_4} 1755 cm^{-1}) and exhibited a red-shifted and intensified n,π^* transition [$\lambda_{max}^{cyclohexane}$ 290 (ϵ 505) and 300 nm (ϵ 535)].[10]

The exclusive formation of saturated products from the oxymercuration of **2** in acetic acid indicates that the participation of two π systems in **2** is even more extensive than those in norbornadiene which gives mainly unsaturated 1,2 adducts from oxymercuration under the same conditions.[5,6] Halpern and coworkers have found that **2** also displaces norbornadiene as a ligand in organometallic compounds.[11] The synthesis and chemical behavior of related compounds are being investigated.

Acknowledgment. The authors wish to thank the National Institutes of Health, Grant No. AM-11676, for the support of this work, and to express their appreciation to Professor Jack Halpern for valuable discussions.

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[11] J. Halpern, unpublished results.

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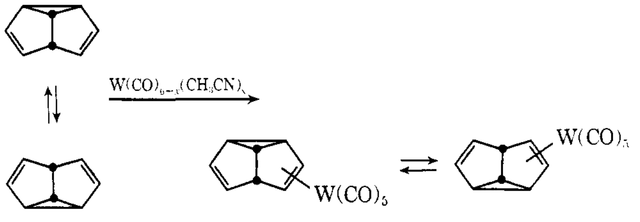
The Tungsten Pentacarbonyl Complex of Semibullvalene. Barrier Height for the Degenerate Cope Rearrangement

Sir:

The rate of the degenerate Cope rearrangement of semibullvalene (**1**) is at present immeasurably fast.[1] The activation energy has been calculated to be 3.6 kcal/mol by the MINDO/2 method.[2] An exciting goal in this area is to modify the structure of semibullvalene so as to increase or decrease the activation energy. A decrease below 3.6 kcal/mol eventually to a negative value poses an interesting philosophical problem. Theoretical calculations, on the other hand, point to modifications which could increase the activation energy. Dewar and Lo[3] using the MINDO/2 method conclude that electron-releasing substituents should destablilze the transition state for the Cope rearrangement. This conclusion agrees with the experimental finding that the activation energy for the Cope rearrangement in octamethylsemibullvalene is 6.4 kcal/mol.[4] Hoffmann and Stohrer[5] have attacked this problem from the point of view of using EHT calculations to determine the effect of substituents not only upon the transition state but also upon the stabilities ot the reactant and product in degenerate and nondegenerate Cope rearrangements of suitably substituted semibullvalene models. So far, except for the example of octamethylsemibullvalene, none of the predictions of Hoffmann and Dewar has been tested experimentally.

We have approached this problem synthetically by attempting to make a metal complex of semibullvalene in which the basic molecule is retained but the divinylcyclopropane part is perturbed by interaction with the metal.

Complexes were obtained with silver nitrate,[6] palladium,[7] and diiron nonacarbonyl.[8] These could not be used for our purpose because they were either too weakly associated, in the case of silver, no longer had the divinylcyclopropane system, in the case of palladium, or possessed a rearranged structure, in the case of iron carbonyl. Success was achieved in the form of the unusual tungsten pentacarbonyl complex **2**;[9] in fact, this is the first example of the isolation of a stable complex between tungsten pentacarbonyl and a tricyclic diene.[10]



1

2

Figure 1 shows the nmr spectrum at room temperature and at −34 and 62°. The relevant nmr parameters are collected in Table I.

The low-temperature spectrum defines the static structure and the high-temperature spectrum agrees with the equilibration process **2a** $\rightleftarrows$ **2b**. In this process the pairs of protons A–F, D–G, and C–E are averaged. The calculated values, (A + F)/2, (D + G)/2, and (C + E)/2 of 4.29, 3.03, and 3.55 ppm are in good agreement with the observed values at room temperature of 4.26, 3.03, and 3.65 ppm. Furthermore, the averaged coupling constants in the high-temperature spectrum agree with prediction. Thus, for proton B, $(J_{AB} + J_{BF})/2$ = 3.1 Hz compares well with the observed splitting of 3.9 Hz.

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[1] Rearrangement persists at −110° on the nmr time; see H. E. Zimmerman, R. W. Binkley, R. S. Givens, G. L. Grunewald, and M. A. Sherwin, *J. Amer. Chem. Soc.*, **91**, 3316 (1969).

[2] M. J. S. Dewar and W. W. Schoeller, *ibid.*, **93**, 1481 (1971).

[3] M. J. S. Dewar and D. H. Lo, *ibid.*, **93**, 7201 (1971).

[4] F. A. L. Anet and F. E. Schenk, *Tetrahedron Lett.*, 4273 (1970).

[5] R. Hoffmann and W.-D. Stohrer, *J. Amer. Chem. Soc.*, **93**, 6941 (1971).

[6] $C_8H_8AgNO_3$, mp 87° dec.

[7] Semibullvalene and potassium tetrachloropalladate(II) in methanol yield a methoxybicyclo[3.3.0]octadienyl π-allyl type complex: R. M. Moriarty, C.-L. Yeh, and K. C. Ramey, to be published.

[8] R. M. Moriarty, C.-L. Yeh, and K. C. Ramey, *J. Amer. Chem. Soc.*, **93**, 6709 (1971).

[9] A solution of W(CO)$_6$ was kept at reflux in 15 ml of CH$_3$CN for 24 hr under nitrogen. The solvent was removed *in vacuo*, a solution of 0.2 g of semibullvalene in 20 ml of hexane was added under nitrogen and the reaction was kept at reflux for 4 hr. The product was isolated by column chromatography on silica gel and 100 mg of a pale yellow-green liquid which solidified upon storage overnight at 0° was obtained. The pure complex has mp 53–54° and the yield based upon consumed semibullvalene is 38%.

Anal. Calcd for $C_8H_8W(CO)_5$: C, 36.44; H, 1.87. Found: C, 36.46; H, 1.84. The mass spectrum showed the parent peak at *m/e* 428 (30%), M − CO, *m/e* 400 (6.5%), M − 2CO, *m/e* 372 (12%), M − 3CO, *m/e* 344 (33%), M − 4CO, *m/e* 316 (83%), M − 5CO, *m/e* 288 (83%), C_8H_8, *m/e* 104 (100%), C_6H_6, *m/e* 78 (96%).

[10] For a recent spectroscopic study of W(CO)$_5$–alkene complexes, see M. Wrighton, G. S. Hammond, and H. B. Gray, *J. Amer. Chem. Soc.*, **93**, 6048 (1971).

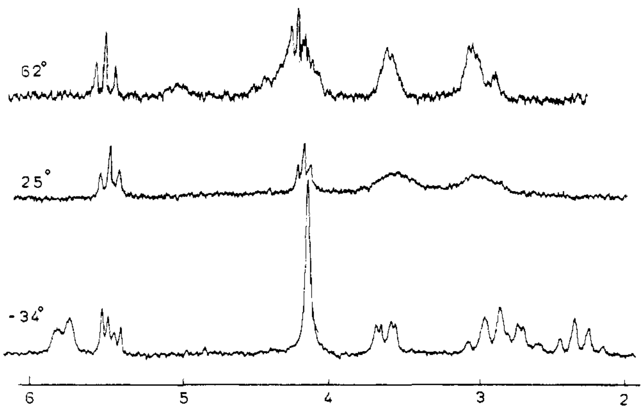
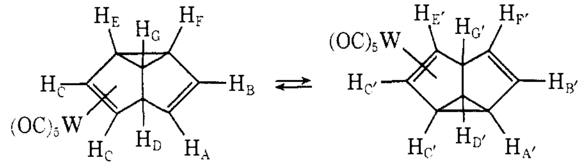


Figure 1. Nmr spectra, 60 MHz, CS_2, of $C_8H_8W(CO)_5$ at various temperatures.

Table I. Nmr Parameters for the Tungsten Carbonyl Semibullvalene Complex[a]



2a ⇄ **2b**

-20°			-30°	
Protons	Chem shifts, ppm	Coupling constants, Hz	Protons	Chem shifts
A	5.82	$J_{AB} = 5.4$		
B	5.51	$J_{AD} = 2.0$	B	5.54, 0.5(J_{AB} + J_{BF}) = 3.1
C	4.18	$J_{BF} = 2.5$	C	4.21
D	3.68	$J_{DC} < 0.5$	D, G	3.06
E	3.00	$J_{DG} = 6.0$	E, C	3.60
F	2.76	$J_{EG} = 5.5$	F, A	4.26
G	2.38	$J_{EF} = 5.5$		
		$J_{EC} < 0.5$		
		$J_{FG} = 5.5$		

[a] In CS_2.

The room temperature spectrum does not show a clear-cut resonance for the C protons which are sp^2 in **2a** and **2b**. However, this is not unreasonable since this region is complicated by the presence of the A–F proton resonances. One final point is that at high temperature the typical spectrum of semibullvalene begins to appear due to decomposition of the complex.

A $\Delta F^{\ddagger}$ value of 12 ± 1 kcal/mol for the process **2a** ⇄ **2b** using $\Delta\nu_{D-G} = 129$ Hz at $t_c = 0° = 273°K$ was obtained. This free energy of activation is approximate because for large values of $\Delta\nu$ it is difficult to determine t_c accurately.

The bonding between the $W(CO)_5$ group and semibullvalene probably involves $p\pi$–$d\pi$ interaction between unoccupied antibonding orbitals of semibullvalene and occupied d orbitals on the tungsten. The carbonyl stretching frequency of **2** occurs at 2079 (w), 1961 (s), and 1949 (s) cm^{-1}. This is very close to the carbonyl peaks reported[10] for $W(CO)_5$ (1-pentene) at 1965 (s) and 1950 (s) cm^{-1}. Tungsten hexacarbonyl absorbs at 1997.5 cm^{-1}. The shift to lower ν_{CO} frequency of the two strong bands at 1961 and 1949 cm^{-1} upon complexation indicates that extensive back donation by the tungsten atom to the double bond of semibullvalene is occurring. Thus, the metal is analogous to an electron-donating substituent and this may be the principal effect in destabilizing the transition state for the Cope rearrangement relative to semibullvalene itself. Of course the ponderal effect of the ligand would have some influence on the magnitude of the barrier height.[11]

Acknowledgment. We wish to thank Badische Anilin- und Soda-Fabrik for a generous gift of cyclooctatetraene.

(11) We wish to thank a referee for pointing this out.

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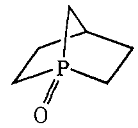
1-Phosphabicyclo[2.2.1]heptane 1-Oxide

Sir:

We wish to report the synthesis and characterization of 1-phosphabicyclo[2.2.1]heptane 1-oxide (**1**), which



1

to our knowledge is the first example of a bicyclo[2.2.1] system which has a phosphorus at a bridgehead position and which contains no other heteroatoms in the ring framework. In fact, despite several attempts,[1–4] even the presumably less strained, analogous 1-phosphabicyclo[2.2.2]octane 1-oxide and its phosphine derivative have never been reported. Examples of both bicyclo[2.2.1] and -[2.2.2] bridgehead phosphorus compounds with other heteroatoms in the ring framework have been prepared.[5–11] Phosphine oxide **1** is of considerable interest since, unlike other closely related systems, pentacovalent, trigonal-bipyramidal compounds and intermediates derived from it are expected to have a relatively high energy barrier to Berry pseudorotation.[12]

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(11) D. W. White and J. G. Verkade, *J. Magn. Resonance*, **3**, 111 (1970).

(12) The three carbons attached to phosphorus cannot be coplanar with the phosphorus and thus cannot serve as the three equatorial substituents in an undistorted trigonal bipyramid derived from 1. Also, no