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]

| | ———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 $\rightleftarrows$ 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]

Robert M. Moriarty,* Chin-Lung Yeh, Ei-Lan Yeh
Department of Chemistry, University of Illinois, Chicago Circle
Chicago, Illinois 60680

Kermit C. Ramey
Research and Development Department
Arco Chemical Company
A Division of Atlantic Richfield Company
Glenolden, Pennsylvania 19036

Received July 3, 1972

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
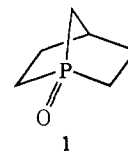
to our knowledge is the first example of a bicyclo[2.2.1] system which has a phosphorus at a bridgehead position and which contains no other heteroatoms in the ring framework. In fact, despite several attempts,[1-4] even the presumably less strained, analogous 1-phosphabicyclo[2.2.2]octane 1-oxide and 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]

(1) W. E. McEwen, C. A. Vanderwerf, A. Bladé-Font, C. B. Parisek, G. Keldsen, D. C. Velez, D. P. Young, K. Kumli, and G. Axelrad, Abstracts of the 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1961, p 96Q.
(2) G. A. Wiley in ref 1, p 40Q; see Quin and Mathewes, ref 3.
(3) L. D. Quin and D. A. Mathewes, *Chem. Ind. (London)*, 210 (1963).
(4) L. D. Quin and H. E. Shook, *J. Org. Chem.*, 32, 1604 (1967).
(5) R. C. Hinton and F. G. Mann, *J. Chem. Soc.*, 2835 (1959).
(6) C. G. Crespan, B. C. McKusick, and T. L. Cairns, *J. Amer. Chem. Soc.*, 82, 1515 (1960); 83, 3432 (1961).
(7) O. Neunhoeffer and W. Maiwald, *Chem. Ber.*, 95, 108 (1962).
(8) B. L. Laube, R. D. Bertrand, G. A. Casedy, R. D. Compton, and J. G. Verkade, *Inorg. Chem.*, 6, 173 (1967).
(9) E. J. Boros, R. D. Compton, and J. G. Verkade, *Inorg. Chem.*, 7, 165 (1968).
(10) E. S. Kozlov, A. I. Sedlov, and A. V. Kirsanov, *J. Gen. Chem. USSR*, 38, 1828 (1968).
(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

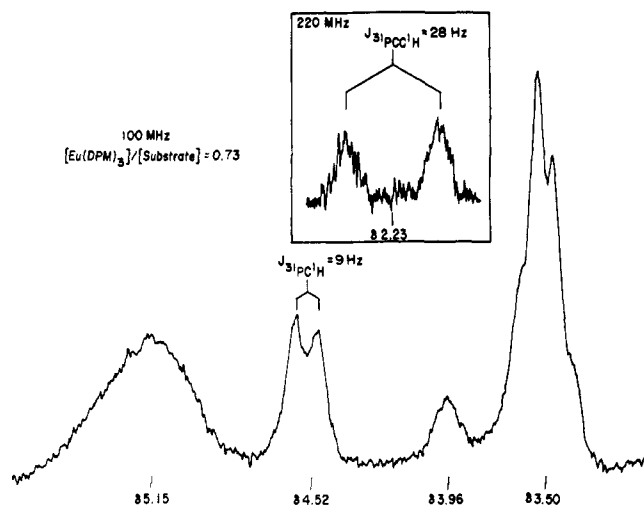Figure 1. Proton nmr spectrum of **1** (CDCl₃) measured at 100 MHz in the presence of 73 mol % Eu(DPM)₃. The insert illustrates a portion of a spectrum of **1** (CDCl₃) measured at 220 MHz in the absence of Eu(DPM)₃ which shows the doublet of multiplets due to the proton on the bridgehead carbon (C₄).

For the synthesis, tricarballylic acid (Aldrich Chemical Co.) was esterified and the resulting triethyl ester[15] was reduced with excess LiBH₄ in dry tetrahydrofuran (THF) to give 3-hydroxymethyl-1,5-pentanediol,[16] bp 165–167° (0.5 mm). This triol was converted to 3-bromomethyl-1,5-dibromopentane[17] by treatment with HBr gas in 72% overall yield (based on tricarballylic acid). A Michaelis–Arbusov reaction with triethyl phosphite and an excess of the tribromide gave, after removal of excess tribromide by vacuum distillation and isolation by column chromatography, a 47% yield of diethyl 5-bromo-3-bromomethylpentylphosphonate (**2**).[18] *Anal.*[19] Calcd for C₁₀H₂₁Br₂O₃P: C, 31.61; H, 5.53; P, 8.16. Found: C, 31.65; H, 5.42; P, 8.39.

2
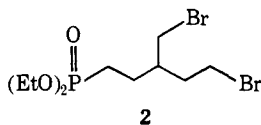
Slow addition under nitrogen of a solution of **2** in dry THF to a refluxing suspension of activated magnesium[20] in THF[21] followed by refluxing for several

two of these carbons may be simultaneously apical. A phosphorane derived from **1** should therefore have five-membered rings spanning apical–equatorial positions and the six-membered ring spanning two equatorial positions. Any pseudorotation of phosphoranes derived from **1** would require placing a five-membered ring in a diequatorial arrangement, an arrangement which had been implicated as being energetically restrictive to pseudorotation in studies conducted on analogous monocyclic pentacovalent systems.[13,14]

(13) D. A. Usher, E. A. Dennis, and F. H. Westheimer, *J. Amer. Chem. Soc.*, **87**, 2320 (1965).

(14) F. H. Westheimer, *Accounts Chem. Res.*, **1**, 70 (1968); K. Mislow, *ibid.*, **3**, 321 (1970).

(15) C. K. Ingold, *J. Chem. Soc.*, **119**, 340 (1921).

(16) R. Lukes, O. Strouf, and M. Ferles, *Chem. Listy*, **50**, 1624 (1956).

(17) V. Prelog and E. Cherkovnikoff, *Justus Liebigs Ann. Chem.*, **525**, 292 (1936).

(18) There are indications from the proton nmr spectrum that this product may contain some of the isomeric diethyl 2-(2-bromoethyl)-4-bromobutylphosphonate.

(19) Microanalyses and the molecular weight determination were performed by the Microanalytical Laboratory, Department of Chemistry, University of California, Berkeley, Calif.

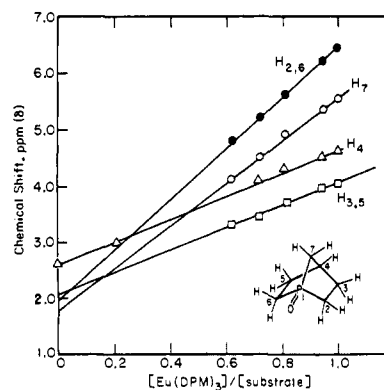(20) A. Mendel, *J. Organometal. Chem.*, **6**, 97 (1966).

Figure 2. A plot of chemical shift *vs.* [Eu(DPM)₃]/[substrate] ratio for various groups of peaks (see Figure 1) in the proton nmr spectrum of **1** (CDCl₃) measured at 60 MHz. In the case of H₄ the chemical-shift data shown are for the downfield half of the doublet.

days gave, after hydrolysis and removal of solvent, a crude oil. An aqueous solution of this oil was extracted first with CCl₄ to remove contaminants and then with CHCl₃. Removal of CHCl₃ gave, after purification by sublimation, **1** as hygroscopic, colorless prisms in 11% yield: mp 207–210° (sealed tube). *Anal.*[19] Calcd for C₆H₁₁OP: C, 55.30; H, 8.46; P, 23.85. Found: C, 54.7; H, 8.3; P, 23.5.

The ir spectrum (CCl₄) showed a strong band characteristic of $>$P=O at 1235 cm⁻¹. The following major mass spectral fragments were identified by accurate mass measurements: m/e 130 (parent ion, C₆H₁₁OP⁺, 96% of base peak), 102 (C₄H₇OP⁺, 98%), 101 (C₄H₆OP⁺, 83%), 84 (C₄H₅P⁺, 77%), 75 (C₂H₄OP⁺, 27%), 55 (C₄H₇⁺, base peak), and 47 (OP⁺, base peak). A molecular weight determination[19] by the osmometric method (CHCl₃) gave a value of 124 ± 6 (calcd, 130).

The proton nmr spectrum at 100 MHz (CDCl₃) showed a complex multiplet at δ 1.52–2.16 (10.5 H) and a symmetric multiplet at 2.50 (0.5 H). At 220 MHz three sets of peaks were discernible: δ 1.74–1.87 (6 H, complex multiplet), 1.96 (4 H, symmetric multiplet), 2.23 (1 H, doublet of multiplets, J_{31PCC1H} = 28 Hz;[22] see insert, Figure 1).

In order to resolve the proton nmr spectrum more completely, the shift reagent tris(dipivalomethano)-europium(III) [Eu(DPM)₃][23] was added to a CDCl₃ solution of **1** in varying amounts. A 100-MHz spectrum at a [Eu(DPM)₃]/[substrate] ratio of 0.73, displayed in Figure 1, shows groups of peaks at δ 3.50 (4.5 H, m), 3.96 (0.5 H, m), 4.52 (2 H, d of d, J_{1HCC1H} ≅ 1.5 Hz, J_{31PC1H} = 9.4 Hz),[22] 5.15 (4 H, m). A plot of chemical shift *vs.* concentration of the shift reagent for each of these multiplets is shown in Figure 2. Using the assumption that the multiplets corresponding to protons closest to the complexed Eu atom should dis-

(21) Analogous Grignard reactions have been employed in the syntheses of acyclic phosphonates, phosphinates, and phosphine oxides [see K. D. Berlin, T. Austin, M. Peterson, and M. Nagabhushanam, *Top. Phosphorus Chem.*, **1**, 17 (1965)]; in addition, G. M. Kosolapoff [*J. Chem. Soc.*, 3739 (1957)] has reported the synthesis of a cyclic phosphinate in very low yield using the Grignard reaction with a phosphonic dichloride.

(22) Coupling to phosphorus was confirmed by ³¹P-decoupling experiments (irradiation at 40.5 MHz, NMR Specialities heteronuclear decoupler).

(23) For previous use of this shift reagent in nmr studies of some phosphine oxides, see Y. Kashman and O. Awerbouch, *Tetrahedron*, **27**, 5593 (1971).
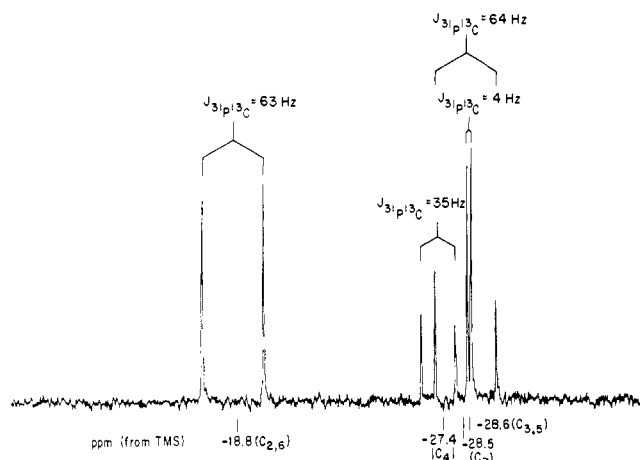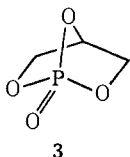
Figure 3. ^{13}C nmr spectrum of 1 (CDCl₃) determined at 24 kG under conditions of proton noise decoupling; scale, parts per million relative to carbons of tetramethylsilane.

play the greatest slope in such a plot,[23] we have made the assignments shown in Figure 2.

The coupling constant (J_{31PC^1H}) of 28 Hz between phosphorus and the proton on the bridgehead carbon (C₄) is unusually large (cf. J_{31PC^1H} for (CH₃CH₂)₃P=O is 16.3 Hz).[24] Inspection of a molecular model shows that the dihedral angle between phosphorus and the coupled proton at C₄ in 1 (sighting down the bond connecting carbons 4 and 7) is rigidly held at 180°. Recent studies[25,26] indicate an angular dependence of J_{31PC^1H} similar to the Karplus relationship for J_{1HCC^1H} values.[27] Also, White and Verkade[11] found an unusually large J_{31POC^1H} value (15.9 Hz) for phosphorus coupling to the bridgehead proton in the analogous phosphate 3.

3

Natural abundance ^{13}C nmr spectra of 1 were determined at both 14 and 24 kG using Fourier transform techniques and proton noise decoupling. The spectrum at 24 kG is shown in Figure 3. Each of the carbons is coupled to phosphorus. As expected, the coupling constants assigned in Figure 3 were shown to be independent of magnetic field strength. The assignments for each of the doublets were made using the assumptions (1) that the coupling constants between phosphorus and the directly attached $C_{2,6}$ and C₇ carbons should be relatively large[28] and nearly identical and (2) that the larger two pairs of peaks should arise from the $C_{2,6}$ and $C_{3,5}$ carbons. Assuming these assignments are correct, the $J_{31PC^{13}C}$ coupling constant between the bridgehead atoms is an order of magnitude greater than the corresponding $J_{31PC^{13}C}$ value between

(24) J. B. Hendrickson, M. L. Maddox, J. J. Sims, and H. D. Kaesz, Tetrahedron 20, 449 (1964).
(25) A. A. Bothner-By and R. H. Cox, J. Phys. Chem., 73, 1830 (1969).
(26) C. Benezra, Tetrahedron Lett., 4471 (1969).
(27) M. Karplus, J. Amer. Chem. Soc., 85, 2870 (1963); S. Sternhell, Quart. Rev., Chem. Soc., 23, 236 (1969).
(28) These observed coupling constants are similar to some previously reported J_{31P13C} values [G. J. Gray and S. E. Cremer, J. Org. Chem., 37, 3458 (1972)].

phosphorus and the $C_{3,5}$ carbons. A possible contributor to this large J value is the presence of three independent bond paths for transmission of coupling between phosphorus and C₇.[11,29] The nature of this effect is the subject of further investigation.

Ronald B. Wetzel, George L. Kenyon*
Department of Chemistry, University of California
Berkeley, California 94720
Received June 24, 1972

A Phosphorus-31 Nuclear Magnetic Resonance Study of Tungsten Carbonyl Complexes Containing Positively Charged Phosphorus Ligands. Observation of $^3J_{WP}$

Sir:

A number of investigators have attempted to assess the electronic influence of the positive charge of a positively charged phosphorus ligand upon the metal-phosphorus bond. Ercolani, Quagliano, and Vallarino have shown with electronic spectra that the positive charge associated with ligands (C₆H₅)₂PCH₂CH₂P⁺-(C₆H₅)₂CH₂C₆H₅[Br⁻] and (C₆H₅)₂PCH₂P⁺(C₆H₅)₂CH₂-C₆H₅[Br⁻] in various zwitterionic complexes has very little influence on the ligating character of these substances.[1] In fact, electronic spectra of complexes of these ligands are superimposable. Berglund and Meek have concluded that the presence of a positive charge in (C₆H₅)₂P⁺(CH₂)₂C(CH₃)CH₂P(C₆H₅)₂[Cl⁻] does not appreciably influence the coordination properties of the ligand.[2,3] Similar conclusions were drawn by Bertrand, Allison, and Verkade for a carbonyl complex of P(OCH₂)₃P⁺CH₃[BF₄⁻].[4] Taylor and Kolodny have suggested that the influence of the positive charge may be more significant in systems in which the cationic charge is separated from the coordinated phosphorus by an unsaturated organic skeleton rather than a saturated one. However, definite conclusions could not be drawn from an infrared and uv-visible study of CoBr₃-(P(C₆H₅)₂C≡CP⁺(C₆H₅)₂CH₂C₆H₅)[Br⁻].[5]

We have recently reported the preparation of complexes of the type (OC)₅WP(C₆H₅)₂(CH₂)ᵧP(C₆H₅)₂ and (OC)₅WP(C₆H₅)₂(CH₂)ᵧP⁺(C₆H₅)₂R[X⁻] (y = 1, 2; R = alkyl; X = anion).[6] From a comparison of the carbonyl stretching frequency data for the quaternized and unquaternized complexes, it was suggested that the positive charge in the γ position has no measurable effect on the metal-phosphorus bond, while in the β

(1) C. Ercolani, J. V. Quagliano, and L. M. Vallarino, Inorg. Chim. Acta, 3, 421 (1969).
(2) D. Berglund and D. W. Meek, J. Amer. Chem. Soc., 90, 518 (1968).
(3) D. Berglund and D. W. Meek, Inorg. Chem., 8, 2603 (1969).
(4) R. D. Bertrand, D. A. Allison, and J. G. Verkade, J. Amer. Chem. Soc., 92, 71 (1970).
(5) R. C. Taylor and R. A. Kolodny, Inorg. Nucl. Chem. Lett., 7, 1063 (1971).
(6) R. L. Keiter and D. P. Shah, Inorg. Chem., 11, 191 (1972).