Nuclear Magnetic Resonance Studies of Some Novel Metal Carbonyl Complexes and Other Derivatives of 2,6,7-Trioxa-1,4-diphosphabicyclo[2.2.2]octane

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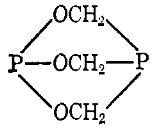
Abstract: The novel coordination properties of the nonchelating bifunctional phosphorus ligand $P(OCH_2)_3P$ have allowed the characterization of $(OC)_5MP(OCH_2)_3P$ and $(OC)_5MP(OCH_2)_3PM(CO)_5$ (M = Cr, Mo, and W); axial $(OC)_4FeP(OCH_2)_3P$, axial $(OC)_4FeP(CH_2O)_3P$, and diaxial $(OC)_4FeP(OCH_2)_3PFe(CO)_4$; $[CH_3P(OCH_2)_3P]BF_4$ and $[P(OCH_2)_3PCH_3]BF_4$; and $[(OC)_5WP(OCH_2)_3PCH_3]BF_4$. The mode of coordination of the ligand in the monometallic and phosphonium compounds was determined from the characteristic changes in the P^{31} chemical shifts and the PH and PP coupling constants. These methods were also used to characterize the unusual nonaxial $(OC)_4FeP(OCH_2)_3P$ (see ref 18). The magnitudes and signs of the ${}^2J_{PH}$, ${}^3J_{PH}$, and ${}^3J_{PP}$ coupling constants in all of the compounds were obtained from the proton nmr spectra using indor techniques where appropriate. The trends in these parameters as the electron-withdrawing power of the fourth group attached to phosphorus increases in the order, electron pair < metal carbonyl fragment < methyl group < chalcogen, are interpreted in terms of the expected changes in nuclear charge of the atoms and s character of the bonds in the ligand. Infrared studies indicate that quaternization of the ligand in $[(OC_5)WP(OCH_2)_3P]$ to form $[(OC)_5P(OCH_2)_3PCH_3]BF_4$ does not detectably alter the overall nature of the tungsten–phosphorus bond.

Unlike most difunctional phosphorus ligands which have been studied, the bicyclic system I[2] is unable to chelate a metal atom because of its rigid geometry. Although the bicyclic diphosphorus ligands II,[3] III,[4]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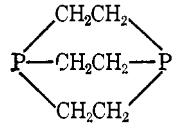
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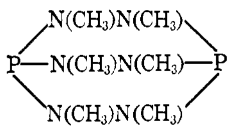
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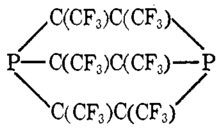
IV

and IV[5] are also known, only a few coordination studies have been reported with these ligands. The complex $ClAuP(CH_2CH_2)_3PAuCl$ and the dimethyl diphosphonium salt of II have been prepared.[3] Several derivatives of III including the dioxide, disulfide, the dimethyl diphosphonium salt, and the bis(borine) adduct have been reported,[4] and more recently the bis(triethylaluminum) adduct was described.[6] Diborane was shown to react with IV at low temperature, but the product is unstable at room temperature. A compound, P_2C_6, has been reported,[7] but it is not certain that the structure is bicyclic.[8] Because of the linear PCCP skeleton of $[(C_6H_5)_2PC]_2$, only complexes in which the ligand bridges to two metal atoms have been obtained.[9] The geometry of 3,3′-bis(diphenylphosphino)biphenyl also appears to allow bridging of two AuCl groups in preference to chelation.[10]

It might be mentioned that chelating phosphorus ligands such as $[(C_6H_5)_2PCH_2]_2$[11] or $[(CH_3)_2PCH_2]_2$[12] are capable of forming a bridge between two metal atoms under certain conditions.

The presence of two chemically different phosphorus coordination sites permits the possibility of linkage isomerism in complexes and phosphonium salts of I. Furthermore, I is capable of coordinating a metal atom on both donor sites as well as functioning as a positively charged ligand if one of the phosphorus atoms is quaternized. The examples for which these possibilities have been realized in this investigation are the linkage isomers ax-$(OC)_4FeP(OCH_2)_3P$ and ax-$(OC)_4FeP(CH_2O)_3P$, and $[CH_3P(OCH_2)_3P]BF_4$ and $[P(OCH_2)_3PCH_3]BF_4$; the complexes of bicoordinated I, $(OC)_5MP(OCH_2)_3PM(CO)_5$ (wherein M = Cr, Mo, or W); and the positive ligand complex $[(OC)_5WP(OCH_2)_3PCH_3]BF_4$.

The disposition of I as formulated in these compounds was determined from their proton and phosphorus nmr spectral parameters. Infrared studies of the carbonyl region of $[(OC)_5WP(OCH_2)_3PCH_3]BF_4$ show that the positive charge on the ligand leads to no detectable change in the phosphorus–metal bond from that in the analogous complex $[(OC)_5WP(OCH_2)_3P]$ in which the ligand I is neutral. The trends in the nmr parameters suggest that the P^{31}–P^{31} spin–spin coupling in I and a variety of its derivatives arises from a "through-bond" rather than from a "through-space" phenomenon across the cage. The progression of this coupling constant (${}^3J_{PP}$) from −37.2 to + 151.3 Hz

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Table I. Nmr Parameters for $P(OCH_2)_3P$, Some Analogous Bicyclic Compounds, and Their Derivatives

	$^2J_{PH}{}^{a}$	$^3J_{PH}{}^{a}$	$\delta H^{1\,b}$	$^3J_{PP}{}^{a}$	$\delta P^{31}O_3{}^{c}$	$\delta P^{31}(C)_3{}^{c}$	Solvent
$P(OCH_2)_3P^{d}$	+8.9	+2.5	4.45	−37.2	−89.78	+66.99	$(CD_3)_2S{=}O$
$P(OCH_2)_3CCH_3{}^{e}$		|2|	3.93		−91.5		CH_3CN
$P(CH_2O)_3CCH_3$	|8.0|^{f}		4.30^{f}			+80.5^{g}	
$(OC)_5CrP(OCH_2)_3P$	+8.5 (8.4)	+5.3 (5.3)	4.87	−3.0 ± 0.3	−154.47	+68.57	CH_3CN
cis-$(OC)_4Cr(P(OCH_2)_3P)_2$	(+)(8.4)^{h}	(+)(5.3)^{h,i}	4.91	−2.4	−157.21	+68.52	CH_3CN
$(OC)_5CrP(OCH_2)_3CC_2H_5{}^{e}$		4.3	4.24		−162		$CDCl_3$
$(OC)_5MoP(OCH_2)_3P$	+8.8 (8.4)	+5.0 (5.2)	4.85	−4.6	−130.82	+68.60	CH_3CN
$(OC)_5MoP(OCH_2)_3CC_2H_5{}^{e}$		4.2	4.20		−136		$CDCl_3$
$(OC)_5WP(OCH_2)_3P$	+8.5 (8.5)	+5.3 (5.5)	5.02	−0.4	−109.09	+68.75	CH_3CN
$(OC)_5WP(OCH_2)_3CC_2H_5{}^{e}$		4.4	4.25		−114		$CDCl_3$
ax-$(OC)_4FeP(OCH_2)_3P$	+8.5 (8.4)	+6.1 (6.1)	5.00	+8.6	−157.44	+71.38	CH_3CN
non-ax-$(OC)_4FeP(OCH_2)_3P$	+8.2 (8.2)	(+) (6.1)^{h}	4.94	+7.6	−159.76	+68.10	CH_3CN
$[CH_3P(OCH_2)_3P]BF_4{}^{j}$	+8.5 (8.7)	+6.6 (6.1)	5.45	+46.2	−51.03	+59.80	CH_3CN
$[CH_3P(OCH_2)_3CCH_3]BF_4{}^{k}$		|5.1|	4.89		−60.15		CH_3CN
$SP(OCH_2)_3P$	+7.6	+7.5	5.11	+48.1	−52.06	+70.89	$(CD_3)_2S{=}O$
ax-$(OC)_4FeP(CH_2O)_3P$	(+) (0.4)^{h}	(+) (2.8)^{h}	4.75	+47.1 ± 2.5	−87.37	−22.42	CH_3CN
$[P(OCH_2)_3PCH_3]BF_4{}^{l}$	−5.4 (5.6)	+3.1 (3.1)	5.15	+114.6	−89.58	−2.56	CH_3CN
$OP(CH_2O)_3CCH_3$	|7.5|		4.40^{m}			−16.00	CD_3CN
$(OC)_5CrP(OCH_2)_3PCr(CO)_5$	(+) (2.0)^{h}	(+) (5.6)^{h}	5.00	+66.1 ± 0.8	−155.52	−8.21	CH_3CN
$(OC)_5MoP(OCH_2)_3PMo(CO)_5$	+2.1 (2.3)	+5.2 (5.4)	4.98	+63.7	−130.97	+18.94	CH_3CN
$(OC)_5WP(OCH_2)_3PW(CO)_5$	(+)^{h} (1.5)	+5.5 ± 0.5 (5.5)	4.82	+73.8	−108.37	+36.34	CH_3CN
$(OC)_4FeP(OCH_2)_3PFe(CO)_4$	(+)(0.4)^{h}	+6.2 (6.3)	5.15	+95.3	−160.40	−22.06	CH_3CN
$OP(OCH_2)_3PO^{n}$	−8.2	+8.3	5.09	+139.1	+18.17	−5.48	$(CD_3)_2S{=}O$
	(−)	(+)		+144.2			CF_3COOH
$[(OC)_5WP(OCH_2)_3PCH_3]BF_4{}^{o}$	−5.6 (5.8)	+6.1 (6.3)	5.70	+143.2	−113.00	−2.98	$(CD_3)_2C{=}O$
$SP(OCH_2)_3PO$	−9.0	+8.2	5.16	+151.3	−49.28	−5.50	$(CD_3)_2S{=}O$

[a] All J values refer to couplings between nuclei in the bicyclic system. Those in parentheses were obtained from the H^1 spectra; all others (except those indicated) were obtained from P^{31} indor spectra and are precise to ±0.4 Hz, except where stated otherwise. All signs were determined from indor spectra on the main proton resonances unless otherwise indicated. [b] δH^1 values are reported with respect to internal tetramethylsilane and are precise to ±0.02 ppm. [c] δP^{31} values are precise to ±0.02 ppm and are reported with respect to external 85% H_3PO_4. [d] $^1J_{CH}$ for this compound was found to be +153.1 ± 0.2 Hz from the H^1 spectrum. Signs of the coupling constants were determined from indor experiments on the C^{13} satellites of the proton resonances. [e] D. G. Hendricker, Ph.D. Thesis, Iowa State University, 1965. [f] Determined in CCl_4; see ref 30. [g] Determined by direct observation in benzene. [h] Only the sign of this coupling constant was determined from the indor spectrum. [i] The H^1 nmr spectrum for this compound is not first order because of the P^{31}–P^{31} coupling between the two PO_3 phosphorus nuclei. The splitting parameter observed in the H^1 spectrum is $N = (^3J_{PH} + {}^5J_{PH})$. However, it is highly probable that $^5J_{PH} = 0$. (See R. K. Harris, *Can. J. Chem.*, **42,** 2275 (1964)), and R. D. Bertrand, F. B. Ogilvie, and J. G. Verkade, *Chem. Commun.*, 756 (1969). [j] $^2J_{CH_3}$ is 18.7 ± 0.2 Hz. [k] $^2J_{CH_3}$ is 19.0 ± 0.5 Hz. [l] $^2J_{PCH_3}$ is 17.0 ± 0.2 Hz. [m] Determined in $CDCl_3$; see ref 30. [n] $^1J_{CH}$ for this compound was found to be +156.7 ± 0.2 Hz from the H^1 spectrum. The signs in parentheses were determined from indor spectra of the C^{13} satellites of the proton resonances. [o] $^2J_{PCH_3}$ is 17.5 ± 0.5 Hz.

through 16 intermediate values in the compounds listed in Table I is explained on the basis of effective nuclear charge increases on phosphorus and increased s character in the bonds of the ligand I.

Experimental Section

The nmr double-resonance experiments were performed on a Varian HR-60 nmr spectrometer operating at 14,000 G modified for field-frequency lock. The instrument is provided with a Hewlett-Packard Model 5100A frequency synthesizer and a Model 5110A frequency synthesizer driver as well as a Hewlett-Packard Model 5243L frequency counter. The V4331 probe is double tuned to accept either the 15.09- or 24.29-MHz perturbing frequencies for C^{13} or P^{31}, respectively, from the frequency synthesizer, simultaneously with the 60.00 MHz from the V-4311 radiofrequency source. The field-frequency locking circuits are activated by phase detection (in dispersion mode) of a sharp internal standard resonance signal. The signal detected is the first upper-field 2-KHz side band produced by a 2-KHz field modulation of the main resonance. Any drift in the field produces a change from zero of the voltage of this signal. The voltage is returned to zero by means of the superstabilizer. The lock-phase detector is tied in with the synthesizer driver. Frequency stabilization is provided by tying the 2-KHz field modulation oscillator circuits, the V-4311 transmitter circuits, the frequency counter clock, and the signal phase detector to either the frequency synthesizer or the synthesizer driver. The spectrometer can be operated in frequency-sweep mode by applying an additional field modulation frequency. Our spectrometer is also equipped with a digital/analog sweep circuit which allows sweeping one decade of the frequency synthesizer which may be used as the secondary frequency source. The time base for the digital/analog sweep circuit is derived from the frequency synthesizer. By the application of a fixed frequency from a very stable oscillator (Hewlett-Packard Model 4202A), it is possible to set the field modulation to a frequency which corresponds to the maximum amplitude of a resonance absorption signal to be investigated. Using the digital/analog sweep unit and synthesizer, frequencies of the other nuclei (P^{31} or C^{13}) can be scanned producing indor spectra of the other nuclei.[13] The stability of the spectrometer is on the order of one part in 10^8 for several weeks.

Infrared spectral data obtained on a Beckman IR-12 spectrometer are given in Table II. Mass spectra were obtained on an Atlas CH-4 single-focusing spectrometer at 70 eV.

$P(OCH_2)_3P$ (I), $SP(OCH_2)_3P$, $OP(OCH_2)_3PO$, and $SP(OCH_2)_3PO$. The ligand I was prepared following our procedure published earlier[2] with the modifications given elsewhere.[14] The chalcogenide derivatives were made from I as described before.[2]

$[P(OCH_2)_3PCH_3]BF_4$ and $[CH_3P(OCH_2)_3P]BF_4$. A solution of 0.5 g (3.3 mmoles) of $[(CH_3)_3O]BF_4$ prepared by the method of Meerwein[15] was dissolved in 20 ml of dry acetonitrile. In this solution was dissolved 0.5 g (3.3 mmoles) of I, and the solution was cooled to −20°. The phosphine isomer crystallized out in 27% yield (mp 140° dec). The mother liquor was found from analysis of the nmr spectrum to contain nearly equal amounts of the two isomers.

$(OC)_5CrP(OCH_2)_3P$ and $(OC)_5CrP(OCH_2)_3PCr(CO)_5$. A mixture of 170 ml of methylcyclohexane, 1.0 g (4.5 mmoles) of $Cr(CO)_6$, and 0.5 g (3.3 mmoles) of I was stirred under a nitrogen atmosphere while irradiating for 2 hr with a 673-A Hanovia lamp. The reaction mixture was filtered and the solvent removed under reduced

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Table II. Infrared Frequency Assignments in the Carbonyl Region

Compound	Frequencies (cm^{-1}) and assignments[a] $A_1{}^2$	$A_1{}^1$	E	Medium
$(OC)_5CrP(OCH_2)_3P$	2077 (w)		1951 (vs)	CH_2Cl_2
$(OC)_5CrP(OCH_2)_3CCH_3$[b]	2082 (w)	1995 (sh)	1960 (vs)	$CHCl_3$
$(OC)_5MoP(OCH_2)_3P$	2077 (w)		1948 (vs)	CH_2Cl_2
$(OC)_5MoP(OCH_2)_3CCH_3$[b]	2085 (w)	2001 (sh)	1962 (vs)	$CHCl_3$
$(OC)_5WP(OCH_2)_3P$	2085 (w)	1907 (sh)	1948 (vs)	CH_2Cl_2
$[(OC)_5WP(OCH_2)_3PCH_3]BF_4$	2085 (w)	1912 (sh)	1947 (vs)	CH_2Cl_2
$(OC)_5WP(OCH_2)_3CCH_3$[b]	2084 (w)	1993 (sh)	1958 (vs)	$CHCl_3$
$(OC)_5CrP(OCH_2)_3PCr(CO)_5$	2073 (m)		1956 (vs)	CH_2Cl_2
$(OC)_5MoP(OCH_2)_3PMo(CO)_5$	2078 (m)		1951 (vs)	CH_2Cl_2
$(OC)_5WP(OCH_2)_3PW(CO)_5$	2077 (m)		1948 (vs)	CH_2Cl_2
ax-$(OC)_4FeP(OCH_2)_3P$	2068 (s)	1991 (s)	1954 (vs)	CH_2Cl_2
ax-$(OC)_4FeP(OCH_2)_3CCH_3$[b]	2065 (s)	1996 (vs)	1965 (vs)	$CHCl_3$
ax-$(OC)_4FeP(CH_2O)_3P$	2065 (s)	1993 (s)	1946 (vs)	CH_2Cl_2
ax-$(OC)_4FeP(CH_2O)_3CCH_3$[c]	2059 (s)	1988 (s)	1949 (vs)	CH_2Cl_2
ax-$(OC)_4FeP(OCH_2)_3PFe(CO)_4$	2068 (s)	1999 (s)	1963 (vs)	CH_2Cl_2
	$A_1{}^2$	$A_1{}^1$	B_1, B_2	
cis-$(OC)_4Cr[P(OCH_2)_3P]_2$	2037 (m)	1946 (sh)	1924 (vs)	CH_2Cl_2
cis-$(OC)_4Cr[P(OCH_2)_3CCH_3]_2$[d]	2043 (m)	1950 (sh)	1925 (vs)	CH_2Cl_2

[a] vs = very strong, sh = shoulder, m = medium, w = weak. Values are precise to ± 2 cm^{-1}. [b] See ref 29. [c] See ref 30. [d] A. C. Vandenbroucke, Jr., D. G. Hendricker, R. E. McCarley, and J. G. Verkade, *Inorg. Chem.*, **7**, 1825 (1968).

pressure. The residue was chromatographed on a silica gel column. The column was prepared and eluted with an equivolume hexane–benzene mixture and the bridged compound was eluted first followed by the complex of lower molecular weight. The parent ions in the mass spectra of the bridged compound (536) and of $(OC)_5CrP(OCH_2)_3P$ (334) were observed.

***cis*-$(OC)_4Cr(P(OCH_2)_3P)_2$.** A mixture of 10 ml of methylcyclohexane, 10 ml of benzene, 0.32 g (2.1 mmoles) of I, and 0.26 g (1.0 mmole) of norbornadienetetracarbonylchromium, prepared by the method of King,[16] was stirred together for 24 hr at room temperature. The solution was cooled to −20° and the liquid decanted. The residue was extracted once with acetonitrile and the extract evaporated to give the desired compound as a white solid in 4% yield. A parent ion peak of 468 was observed in the mass spectrum of the compound.

$(OC)_5MoP(OCH_2)_3P$ and $(OC)_5MoP(OCH_2)_3PMo(CO)_5$. A mixture composed of 60 ml of methylcyclohexane, 2.0 g (7.6 mmoles) of $Mo(CO)_6$, and 1.0 g (6.6 mmoles) of I was stirred under nitrogen atmosphere while refluxing for 7 hr. The solvent was removed under reduced pressure and the white residue chromatographed on a silica gel column prepared and eluted in the same manner as for the chromium analogs. A 20% yield (based on I) was obtained for $(OC)_5MoP(OCH_2)_3P$, and a 1% yield (based on $Mo(CO)_6$) was obtained for the bridged complex. A mass spectrum of the bridged complex revealed a parent peak at the calculated mass of 628 based on Mo^{98}, and the $(OC)_5MoP(OCH_2)_3P$ complex showed a parent ion of 390 in its mass spectrum.

Anal. Calcd for $MoC_8H_6O_8P_2$: C, 24.76; H, 1.56; P, 15.96. Found: C, 24.98; H, 1.74; P, 15.96.

$(OC)_5WP(OCH_2)_3P$ and $(OC)_5WP(OCH_2)_3PW(CO)_5$. A mixture of 50 ml of benzene, 0.26 g (1.7 mmoles) of I, and 0.72 g (1.7 mmoles) of $(OC)_5WNH_2C_6H_5$, prepared by the method of Angelici,[17] was stirred together for 24 hr at room temperature. The white solid remaining after evaporation of the solvent was chromatographed on a silica gel column with a 50% hexane–benzene solution. A trace of the bridged complex was eluted first, followed closely by the $(OC)_5WP(OCH_2)_3P$. The parent ion of mass 476 based on W^{184} was observed in the mass spectrum of the latter compound. The $(OC)_5WP(OCH_2)_3P$ was obtained in 25% yield.

The bridged compound was prepared in better yield (23%) by using a lower ligand to metal ratio (1:2). Thus a mixture of 20 ml of benzene, 0.15 g (1 mmole) of I, and 0.84 g (2 mmoles) of $(OC)_5WNH_2C_6H_5$ was treated as described above. The crude white product obtained upon evaporation under reduced pressure was chromatographed as in the previous separation to give the pure product. A mass spectrum of this bridged complex revealed a parent ion peak at mass 800.

$[(OC)_5WP(OCH_2)_3PCH_3]BF_4$. A mixture of 50 ml of dichloromethane, 0.48 g (1 mmole) of $(OC)_5WP(OCH_2)_3P$, and 0.15 g (1 mmole) of $[(CH_3)_3O]BF_4$ was stirred under nitrogen for 2 hr at room temperature. The solvent was removed with a stream of dry nitrogen. The solid was recrystallized from acetonitrile to give a 10% yield of the complex.

ax-$(OC)_4FeP(OCH_2)_3P$, ax-$(OC)_4FeP(CH_2O)_3P$, non-ax-$(OC)_4$-$FeP(OCH_2)_3P$, and ax-$(OC)_4FeP(OCH_2)_3P$-ax-$Fe(CO)_4$. The preparation and characterization of these compounds are reported elsewhere.[18]

Results

The use of the double resonance experiment[19] in determining the relative signs of coupling constants has been described by others.[20,21] The application of this technique to the compound $OP(OCH_2)_3PO$ is now described as an example. The proton nmr spectrum of those molecules without C^{13} nuclei consists of a doublet of doublets in which ${}^2J_{PH} = 8.2$ Hz and ${}^3J_{PH} = 8.3$ Hz. The results of the indor experiments necessary to relate the signs of these couplings to ${}^3J_{PP}$ are shown in Figure 1. It can be seen from tickling in the phosphate P^{31} region that the highest frequency H^1 resonance is perturbed by irradiating the low-frequency member of the phosphate P^{31} doublet,[22] while the opposite is true for the lowest frequency H^1 line. Thus, ${}^2J_{PH}$ is opposite in sign to ${}^3J_{PP}$. Tickling in the phosphine oxide P^{31} region reveals that the highest frequency member of the H^1 spectrum is perturbed by irradiating the high-frequency member of the phosphine oxide P^{31} doublet,[22] while the opposite is true for the lowest frequency line. Consequently, ${}^3J_{PH}$ is the same sign as ${}^3J_{PP}$. Since ${}^2J_{PH}$ is opposite in sign to ${}^3J_{PP}$, ${}^2J_{PH}$ is opposite in sign to ${}^3J_{PH}$. The couplings ${}^3J_{PH}$ and ${}^2J_{PH}$ are given by the splittings in the H^1 spectra, while ${}^3J_{PP}$ is the spacing between the centers of the members of the phosphate P^{31} or phosphine oxide P^{31} doublets.[22] The chemical shifts for the two P^{31}

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(21) (a) E. F. Friedman and H. H. Gutowsky, *ibid.*, **45**, 3158 (1966); (b) D. H. Whiffen, *ibid.*, **47**, 1565 (1967).

(22) Each member of this doublet is split into a septet due to the six equivalent methylene protons, and five of the theoretical lines are observed.

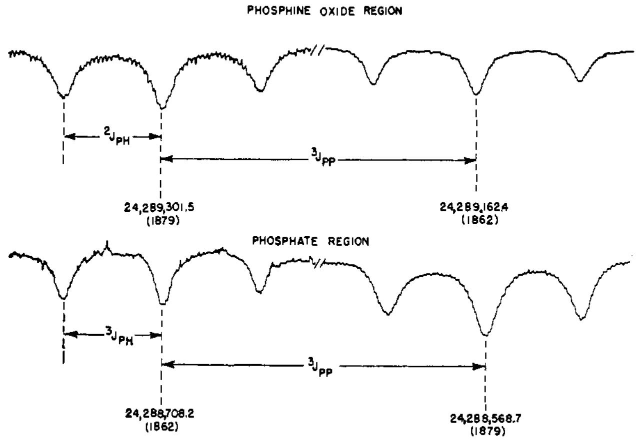

Figure 1. Indor spectra obtained for $OP(OCH_2)_3PO$, in which two of the lines in the proton spectrum are observed (nonsimultaneously) while irradiating in the phosphine oxide and phosphate P^{31} regions. The two nine-digit numbers in each spectrum refer to the frequencies of the center members of the two septets arising from coupling to the protons. In each case, five members of the septet could be seen, the outer members being too weak to observe. Only the center three members of each septet are shown. The numbers in parentheses are the modulation frequencies of the proton lines employed in the indor experiment when the spectrometer was locked on benzene.

nuclei were related to 85% H_3PO_4 by determining the P^{31} frequency of the latter compound relative to the H^1 resonance of the internal standard benzene. This was done by first observing that the center of the P^{31} resonance of $P(OCH_3)_3$, as observed by an indor experiment, occurred at 24,292,490.3 Hz, when the field was such that benzene absorbs at 60,002,000.0 Hz. Assuming that the P^{31} chemical shift of $P(OCH_3)_3$ is 140.00 ppm downfield[23] (or toward higher frequency at fixed field) from 85% H_3PO_4, then the P^{31} frequency of 85% H_3PO_4 is at 24,289,089.9 Hz when the spectrometer is locked at 60.002 MHz on benzene. The P^{31} chemical shifts for each P^{31} nucleus of all the compounds which are reported, except for $OP(OCH_2)_3PO$, were calculated by taking the difference between the H_3PO_4 frequency and the frequency of the center of the P^{31} doublet determined by a pair of indor experiments and dividing by the former frequency. For compound $OP(OCH_2)_3PO$, the ratio of the difference in chemical shifts of the phosphorus nuclei to $^3J_{PP}$ is $\sim$2.5, and so the P^{31} chemical shifts were determined by an AB analysis,[24] using the positions of the four bands observed in the P^{31} indor experiments. Using the methyl C^{13} resonance in acetic acid as an external reference, the C^{13} chemical shifts were calculated in the same manner as the P^{31} shifts.

In principle, it is possible to employ the C^{13} satellite resonances in the H^1 spectrum to relate the previously discussed coupling constants in an absolute fashion to $^1J_{CH}$.[25] From such experiments $^1J_{PC}$ and $^2J_{PC}$ are also obtained. Limited quantities of some of the compounds and insufficient solubilities for others precluded application of the C^{13} satellite method in most cases. The two compounds for which this method was feasible were $OP(OCH_2)_3PO$ and $P(OCH_2)_3P$. The analyses were hampered, however, by broadening of the C^{13} satellites by long-range coupling, presumably from other methylene protons. Molecular models show quite clearly that each C^{13} methylene proton in a molecule containing a C^{13} methylene carbon is in a "W" configuration with a chemically and magnetically different proton on each of the other C^{12} methylene carbons. This configuration is known to be conducive to four-bond coupling and gives rise to a coupling constant of about 2 Hz[26] in $P(OCH_2)_3P$ and $OP(OCH_2)_3PO$.

In the C^{13} satellites of the proton spectrum of $P(OCH_2)_3P$, only a broad doublet ($^2J_{PH}$ = 8 Hz) is seen because of the long-range coupling, and it was not possible to distinguish the two spin states of the phosphite P^{31} nucleus. Attempts to decouple the $C^{12}H_2$ protons were accompanied by loss of the field-frequency lock resulting from phase detector overload, which in turn arose from the high modulation index required. Using the normal H^1 spectrum, $^3J_{PH}$, $^2J_{PH}$, and $^3J_{PP}$ could be related as was described above in detail for $OP(OCH_2)_3PO$. With the C^{13} satellites in the proton spectrum, the signs of these couplings could be assigned absolutely since $^2J_{PH}$ could be related to $^1J_{CH}$.[27] Because $^3J_{PH}$ and $^2J_{PH}$ are both sufficiently large in $OP(OCH_2)_3PO$, the two doublets in the C^{13} satellite proton spectra were resolved in spite of the long-range four-bond proton–proton coupling, and all the coupling signs could be related absolutely to $^1J_{CH}$ (Table I).

Discussion

The symmetries of the metal complexes of I[28] can be determined from the characteristic infrared absorptions in the carbonyl region which were assigned by analogy to those for the analogous $P(OCH_2)_3CCH_3$ and $P(CH_2O)_3CCH_3$ complexes (Table II). Of the three and six possible bands in the $(OC)_5M(I)$ and $(OC)_5M(I)M(CO)_5$ systems, respectively (where M = chromium, molybdenum, and tungsten), only the $A_1{}^2$ and E modes were resolved. The composition and molecular weights of all these systems were confirmed by observation of the parent ion peaks in their mass spectra. The symmetries of the two axial linkage isomers of the iron carbonyl complex and of the unusual nonaxial isomer are discussed elsewhere.[18] The *cis* configuration of the disubstituted chromium complex is supported by the observation of

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(23) V. Mark, C. H. Dungan, M. M. Crutchfield, and J. R. Van Wazer in "Topics in Phosphorus Chemistry," Vol. 5, M. Grayson and E. J. Griffith, Ed., Interscience Publishers, 1967, p 227.

(24) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959.

(25) D. A. Buckingham and K. A. McLauchlan in "Progress in Nuclear Magnetic Resonance Spectroscopy," Vol. II, J. W. Emsley, J. Feeney, and L. H. Sutcliffe, Ed., Pergamon Press, Oxford, 1967, p 63.

(26) This estimate stems from the results of measurements of similar couplings in six-membered ring phosphorus systems: D. W. White, R. D. Bertrand, G. K. McEwen, and J. G. Verkade, submitted for publication.

(27) It was also possible to relate $^1J_{PC}$ to $^1J_{CH}$ whereas this was not the case with $^2J_{PC}$ because of the broadening.

(28) We propose that the complexes be named as bicyclo[2.2.2]-octane derivatives in order to unambiguously locate the metal moiety on the ligand. Thus, since I is named 2,6,7-trioxa-1,4-diphosphabicyclo-[2.2.2]octane, we propose that ax-$(OC)_4FeP(CH_2O)_3P$ be named 4-tetracarbonyliron(0)-axial)-2,6,7-trioxa-1,4-diphosphabicyclo[2.2.2]octane, whereas non-ax-$(OC)_4FeP(OCH_2)_3P$ be named 1-(tetracarbonyliron-(0)-non-ax)-2,6,7-trioxa-1,4-diphosphabicyclo[2.2.2]octane. Similarly, $[(OC)_5WP(OCH_2)_3PCH_3]BF_4$ would be 1-(pentacarbonyltungsten-(0))-4-methyl-2,6,7-trioxa-1,4-diphosphabicyclo[2.2.2]octane fluoroborate, and *cis*-$(OC)_4Cr[P(OCH_2)_3P]_2$ would be 1-(tetracarbonylchromium(0)-*cis*)bis-(2,6,7-trioxa-1,4-diphosphabicyclo[2.2.2]octane). In all cases, the number preceding the metal fragment represents its location on the ligand. The placement of "axial," "nonaxial," and "*cis*" in the name is somewhat arbitrary, but would seem appropriately associated with the metal fragment, since it is indicative of the geometry on the metal.

three of the characteristic four carbonyl modes (A_1^1, A_1^2, and B_1, B_2) and the composition and molecular weight are confirmed by its mass spectrum. Because most of the complexes showed evidence of decomposition on standing, commercial elemental analyses were not deemed reliable because of the time involved. The analysis of the stable $(OC)_4MoP(OCH_2)_3P$ complex, however, is in agreement with its formulation as a monosubstituted complex.

The mode of attachment of I to the metal cannot be unambiguously assigned on the basis of positions of the CO bands. This was brought to our attention by the observation that the bridged group VI carbonyl complexes showed only two unresolvable carbonyl infrared bands when at least four were expected on the basis of two different phosphorus donor sites. It is unlikely that exchange of metal carbonyl fragments on the ligand sites accounts for this result since, for example, in a mixture of $(OC)_5WP(OCH_2)_3PW(CO)_5$ and free ligand, the proton resonances of both species are present and that for the ligand occurs at the normal chemical shift observed for a solution of pure I. The nmr studies are described later. In the iron carbonyl axial linkage isomers, the CO frequencies are sufficiently different for a tentative linkage isomer assignment to be made on the basis of the infrared data obtained previously (see Table II) for the $P(OCH_2)_3CCH_3$ and $P(CH_2O)_3CCH_3$ analog, wherein the phosphite complex possesses the higher carbonyl stretching frequencies. This was also observed to be the case for the $Ni(CO)_3L$, $Ni(CO)_2L_2$, and *trans*-$(OC)_3FeL_2$ complexes of $P(OCH_2)_3CCH_3$[29] and $P(CH_2O)_3CCH_3$.[30]

The validity of the assignments of the P^{31} chemical shifts for the two chemically nonequivalent phosphorus nuclei in $P(OCH_2)_3P$, $SP(OCH_2)_3P$, $OP(OCH_2)_3PO$, and $SP(OCH_2)_3PO$ was shown previously[2] from a comparison with the P^{31} chemical shifts observed for $P(OCH_2)_3CCH_3$ (−91.5 ppm),[31] $OP(OCH_2)_3CCH_3$ (+7.9 ppm),[31] and $SP(OCH_2)_3CCH_3$ (−57.4 ppm).[31] The last value in conjunction with that now determined for $OP(CH_2O)_3CCH_3$ (+6.00 ppm) supports the present assignments made from indor experiments for the P^{31} nuclei in $SP(OCH_2)_3PO$ which was not sufficiently soluble for measurement of its P^{31} spectrum directly.[2] It should be noted that the δP^{31} values for the "phosphine" ($P(C)_3$) phosphorus in $P(OCH_2)_3P$ and $SP(OCH_2)_3P$ and the "phosphine oxide" phosphorus in $SP(OCH_2)_3PO$ and $OP(OCH_2)_3PO$ are now established more firmly by the δP^{31} values for $P(CH_2O)_3CCH_3$ and $OP(CH_2O)_3CCH_3$ shown in Table I.

The site of coordination in $P(OCH_2)_3P$ for the complexes was determined from a comparison of the δP^{31} values with those of the analogous $P(OCH_2)_3CCH_3$ complexes and the free ligand I (Table I). For example, only a small change in $\delta P^{31}(C)_3$ occurs from I (+66.99 ppm) to $(OC)_5CrP(OCH_2)_3P$ (+68.57 ppm), while the 65-ppm downfield shift in the $\delta P^{31}O_3$ value to −154.47 ppm in the complex is comparable to that observed for the shift from $P(OCH_2)_3CCH_3$ (−91.5 ppm) to $(OC)_5CrP(OCH_2)_3CCH_3$ (− 162 ppm).

The linkage isomerism in the two axial $(OC)_4Fe$ (I) complexes is clearly supported by the δP^{31} data. In axial $(OC)_4FeP(OCH_2)_3P$ the $\delta P^{31}(C)_3$ and $\delta P^{31}O_3$ values of −157.44 and +71.38 ppm, respectively, are consistent with a coordinated phosphite and an uncoordinated phosphine moiety of I. The reverse situation obtains in axial $(OC)_4FeP(CH_2O)_3P$, as the $\delta P^{31}O_3$ value of −87.37 ppm (uncoordinated phosphite) and the $\delta P^{31}(C)_3$ value of −22.42 ppm (coordinated phosphine) suggest. The best evidence for these assignments comes from the values of $\delta P^{31}O_3$ (−160.40 ppm) and $\delta P^{31}(C)_3$ (−22.06 ppm) in diaxial $(OC)_4FeP(OCH_2)_3PFe(CO)_4$ in which both phosphorus nuclei must be coordinated. The geometrical isomer nonaxial $(OC)_4FeP(OCH_2)_3P$ apparently contains I coordinated through the phosphite end on the basis of the δP^{31} values. Further evidence for the fact that it is isomeric with the axial structure comes from the δP^{31} and $^3J_{PP}$ values, which are similar, but definitely not equal, considering the relatively small experimental errors in the measurements.

The assignment of the linkage isomerism of I in the phosphonium salts was made by comparing the δP^{31} values for $[CH_3P(OCH_2)_3P]BF_4$ ($\delta P^{31}O_3$ = −51.03 ppm, $\delta P^{31}(C)_3$ = +59.80 ppm), $[P(OCH_2)_3PCH_3]BF_4$ ($\delta P^{31}O_3$ = −89.58 ppm, $\delta P^{31}(C)_3$ = −2.56 ppm), I ($\delta P^{31}O_3$ = −89.78 ppm, $\delta P^{31}(C)_3$ = +66.99 ppm), and $[CH_3P(OCH_2)_3CCH_3]BF_4$ ($\delta P^{31}O_3$ = −60.15 ppm). The small effect on the chemical shift of one of the phosphorus nuclei caused by quaternizing the other in each case seems to indicate that a positive charge at one end of the molecule does not significantly affect the electronic properties of the phosphorus at the opposite end. This is particularly evident in the lack of any significant change in the frequencies of the carbonyl modes from $(OC)_5WP(OCH_2)_3P$ to $[(OC)_5WP(OCH_2)_3PCH_3]BF_4$ (Table II). These results suggest that electronic changes due to quaternization are rather localized near the phosphorus atom coordinated to the carbonium ion. Similar conclusions were drawn by Berglund and Meek[32] for several cationic transition metal complexes of the cationic ligand $(C_6H_5)_2P^+(CH_2)_2C(CH_3)CH_2P(C_6H_5)_2$, in which the donor phosphorus atom is one bond further removed from the quaternized phosphorus than in the $P(OCH_2)_3P^+CH_3$ cation.

A discussion of the trends in the various coupling constants is facilitated by the division of the compounds in Table I into three classes (class A, $YP(OCH_2)_3P$; class B, $P(OCH_2)_3PY$; class 3, $YP(OCH_2)_3PY$), wherein the substituent group on the phosphorus in question can be an electron pair, a metal fragment, a methyl carbonium ion, or a chalcogen atom. For each class, plots have been constructed of $^3J_{PP}$ *vs.* $^3J_{PH}$ (Figure 2) and $^3J_{PP}$ *vs.* $^2J_{PH}$ (Figure 3) in order to reveal the various trends in these couplings which will be discussed in the following paragraphs. It should be noted that for each of the class C compounds, Y is the same Lewis acid except for $(OC)_5WP(OCH_2)_3P^+CH_3$ and $SP(OCH_2)_3PO$.

From Figure 2 it is seen that $^3J_{PH}$ increases substantially (∼5 Hz) in positive magnitude for classes A and C, but only slightly (∼0.5 Hz) for class B, as the Lewis acidity of the Y group increases in the order electron pair < methyl < chalcogen. This is not unexpected in

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(29) J. G. Verkade, R. E. McCarley, and D. G. Hendricker, *Inorg. Chem.*, 4, 228 (1965).

(30) E. J. Boros, R. D. Compton, and J. G. Verkade, *ibid.*, 7, 165 (1968).

(31) J. G. Verkade and R. W. King, *ibid.*, 1, 948 (1962).

(32) D. Berglund and D. W. Meek, *J. Am. Chem. Soc.*, 90, 518 (1968).

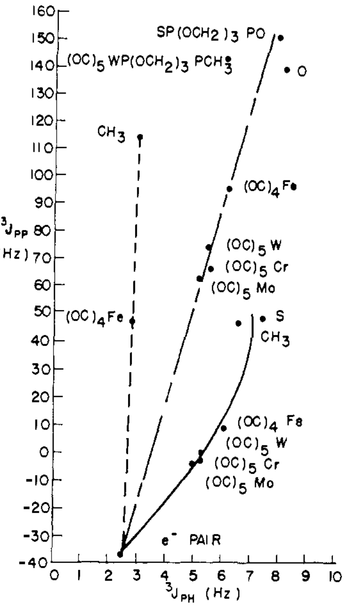

Figure 2. Plot of ${}^3J_{PP}$ *vs.* ${}^2J_{PH}$ for $YP(OCH_2)_3P$ (———), $P(OCH_2)_3PY$ (- - - -), and $YP(OCH_2)_3PY$ (— – —), where the Y groups are those indicated adjacent to each point.

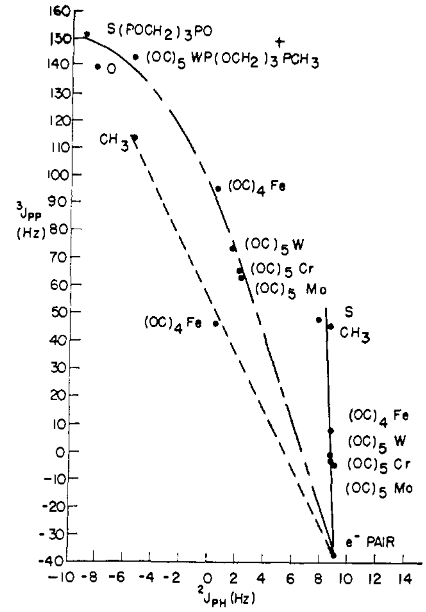

Figure 3. Plot of ${}^3J_{PP}$ *vs.* ${}^2J_{PH}$ for $YP(OCH_2)_3P$ (———), $P(OCH_2)_3PY$ (- - - -), and $YP(OCH_2)_3PY$ (— – —), where the Y groups are those indicated adjacent to each point.

view of the increase in s character in the internal P–O bonds of the ligand and the rise in effective positive charge on the nuclei of the cage (particularly the coordinated PO_3 phosphorus), which would accompany an increase in Lewis acidity of Y. The very much smaller rise in ${}^3J_{PH}$ in the class B compounds might stem from the fact that the $P(C)_3$ phosphorus is coordinated to Y and this donor site is more remote from the POCH bond system through which ${}^3J_{PH}$ is transmitted. Extension of the explanation given for the rise in ${}^3J_{PH}$ in the class A and C compounds to the very small rise in the class B compounds must be viewed with some caution, because of the small range of this parameter in the latter compounds (~0.5 Hz) and the error in the measurements (0.1–0.2 Hz). The correlation of effective nuclear charge and hybridization changes with coupling constants in bicyclic phosphorus molecules and their derivatives has been discussed in other publications, and the arguments will not be repeated here.[33–35]

Figure 3 reveals that ${}^2J_{PH}$ becomes negative upon increasing the Lewis acidity of Y over a range of *ca.* 15 Hz for classes B and C, whereas a range of less than *ca.* 1 Hz is noted for the compounds in class A. Recently[36] we cited experimental evidence from nmr studies which strongly suggested a sign change of this coupling in a similar series of compounds from $P(CH_2O)_3CCH_3$ to $(OC)_4FeP(CH_2O)_3CCH_3$ to $OP(CH_2O)_3CCH_3$, but we were unable to determine the absolute signs. The present data firmly support our previous postulate of a sign change in ${}^2J_{PH}$. Manatt and coworkers[37] discussed sign data obtained on other phosphine derivatives, which indicated that as the s character in the P–C bonds increases due to increasing electronegativity of the Y group on phosphorus, PCH coupling (${}^2J_{PH}$) should become less positive or more negative. We find the data depicted in Figure 3 in good agreement with this postulate for the class B and C systems.

Values of ${}^2J_{PH}$ for all the members of class A fall between +7.6 and +8.9 Hz. Gagnaire and coworkers[38] have found that there is a correlation which can be made in a large variety of phosphines between ${}^2J_{PH}$ and the dihedral angle made by a plane containing the P, C, and H atoms, the plane containing the C–P bond, and the threefold axis of the PC_3 bond system. The expected value of ${}^2J_{PH}$ for the class A compounds and $P(CH_2O)_3CCH_3$ according to their plot, is +5 Hz, which is somewhat below the +7.6–+8.9 Hz we observe for the former and the +8.0 Hz[30] for the latter. The small discrepancy can be explained on the basis of studies carried out by Pople and Bothner-By[39] and Manatt.[37] From a molecular orbital treatment of the HCH system in hydrocarbon derivatives and a consideration of the available nmr data in these systems, Pople and Bothner-By[39] have concluded that increasing the electronegativity of a substituent on carbon should increase the s character in the H–C bonds and thus increase ${}^2J_{HH}$ toward more positive values. The same conclusion was reached by Manatt and coworkers[37] for substituents on carbon in PCH systems from a study of the signs of ${}^2J_{PH}$ in phosphine systems. Thus the lack of consistency of the ${}^2J_{PH}$ values in our systems with those of the phosphines examined by Gagnaire, *et al.*[38] (which contained only hydrocarbon substituents), could be due to the fact that the $P(C)_3$ carbons in our compounds are bonded to electronegative oxygen systems such as YPO_3 groups in class A and a CH_3CO_3 group in $P(CH_2O)_3CCH_3$. Such groups would tend to raise a positive ${}^2J_{PH}$[37] value above the 5 Hz predicted for, say, $P(CH_2CH_2)_3CCH_3$ or $P(CH_2CH_2)_3P$. The former com-

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(33) R. L. Keiter and J. G. Verkade, *Inorg. Chem.*, **8**, 2115 (1969).

(34) J. G. Verkade, T. J. Huttemann, M. K. Fung, and R. W. King, *ibid.*, **4**, 83 (1965), and references therein.

(35) F. Ogilvie, R. J. Clark, and J. G. Verkade, *ibid.*, **8**, 1904 (1969), and references therein.

(36) E. J. Boros, R. D. Compton, and J. G. Verkade, *ibid.*, **7**, 165 (1968).

(37) S. L. Manatt, G. L. Juvinall, R. I. Wagner, and D. D. Elleman, *J. Am. Chem. Soc.*, **88**, 2689 (1966), and references therein.

(38) J. P. Albrand, D. Gagnaire, and J. B. Robert, *Chem. Commun.*, 1469 (1968).

(39) J. A. Pople and A. A. Bothner-By, *J. Chem. Phys.*, **42**, 1339 (1965).

pound is as yet unknown whereas the nmr parameters for the latter have not been reported. A second contributing factor to the somewhat large $^{2}J_{PH}$ values in our compounds might be the slightly less-than-normal CPC bond angles (*i.e.*, less s character in the P–C links) due to constraint. Gagnaire, *et al.*,[38] assumed a constant CPC angle of 100° in their correlation work. The reason for the small rise in $^{2}J_{PH}$ with rising electron-withdrawing power of the Y group in the class A compounds is not apparent at this time.

The values and signs of the vicinal $^{3}J_{PP}$ couplings for the 17 compounds in Table I represent the first systematic study of this coupling constant. While our studies were in progress, McFarlane[40] reported that $^{3}J_{PP}$ in I was -38.1 ± 0.4 Hz, which agrees well with our value (Table I). Figure 2 (or 3) shows that this coupling constant increases markedly from negative to positive values as the Lewis acidity of the Y group increases in the order electron pair < metal carbonyl fragment < methyl < chalcogen for each class of compounds. This trend parallels those discussed above for the rise in $^{2}J_{PH}$ and $^{3}J_{PH}$, and the same arguments based on effective nuclear charge and hybridization changes in the bicyclic portion of these systems used to interpret the latter results are felt to apply here. It is interesting that $^{3}J_{PP}$ is more sensitive to coordination of the $P(C)_3$ phosphorus than the PO_3 phosphorus of I. This may arise from the greater polarizability of a more basic "phosphine" phosphorus lone pair by the Lewis acid moiety. Polarizing both phosphorus lone pairs (class C) augments the $^{3}J_{PP}$ coupling over that in analogous compounds in classes A and B as expected. Although no theoretical basis for vicinal P^{31}–P^{31} couplings has been put forth, the data reported here suggest that $^{3}J_{PP}$ values become more positive with increasing s character and effective nuclear charges in I.

The parallel trends among the various coupling constants in all three classes of compounds are made more significant by the fact that the structural rigidity of the systems discussed here eliminates rotational averaging of couplings which could vary among the compounds studied, and so these effects need not be considered in the coupling mechanism. It remains, however, to consider the possibility of a "through-space" P^{31}–P^{31} spin–spin coupling involving the phosphorus nonbonding orbital lobes which lie inside the bicyclic structure along the threefold axis of the molecule. The distance between the phosphorus atoms is probably at least 2 Å which would seem to mitigate against such a mechanism. Moreover it would be difficult to see how this coupling could rise positively with the increasing Lewis acidity of Y as observed, inasmuch as the phosphorus nonbonding hybrid lobe(s) would be expected to lose s character. A larger effect on the PH couplings of the uncoordinated phosphorus atoms in classes A and B might also have been expected. We tentatively conclude, therefore, that a through-space coupling mechanism need not be invoked presently. The observation that quaternizing the uncoordinated phosphorus in $(OC)_5WP(OCH_2)_3P$ with a carbonium ion did not visibly alter the CO stretching frequencies in the complex indicates that the interaction of the phosphorus lobes inside the cage, if any, was not sufficient to allow inductive effects to change the donor properties of the phosphorus coordinated to the tungsten.

An idea of the effect of a caged structure on the magnitude of $^{3}J_{PP}$ can be gained from the report that even with the π system in *trans*-$(CH_3O)_2P(O)CH{=}CHP(O)(OCH_3)_2$, $^{3}J_{PP}$ is only 37.2 Hz.[41] Furthermore, Finer and Harris[42] recently have determined from H^1 nmr line-shape analysis that $^{3}J_{PP}$ in $ClP(N(CH_3)N(CH_3))_2PCl$ is small compared to the approximately 80 Hz found for III. We conclude that the augmentation of $^{3}J_{PP}$ in the bicyclic systems is best ascribed to the three independent bond paths available for transmission of coupling from one phosphorus to the other in contrast to the limitation to only one or two such paths imposed by open-chain or monocyclic systems.

The signs of the respective couplings of phosphorus to C^{13} in I and its dioxide derivative agree with those reported by McFarlane[43] for $P(OCH_3)_3$, $OP(OCH_3)_3$, $P(CH_3)_3$, $SP(CH_3)_3$, and $SeP(CH_3)_3$. The $^{1}J_{PC}$ value of -15 ± 1 Hz for I is only about 1 Hz larger in magnitude than the -13.6-Hz value reported for the same coupling in $P(CH_3)_3$.[43] The value of this coupling in the dioxide derivative of I is $+67.1 \pm 0.7$ Hz which is 11.0 Hz larger than the value of 56.1 Hz reported for $SP(CH_3)_3$ and 18.6 Hz larger than the value reported for $SeP(CH_3)_3$.[43] The value of -8.5 ± 0.7 Hz for $^{3}J_{PC}$ in the dioxide derivative of I is close to the value of -5.8 for this coupling in $OP(OCH_3)_3$.[43]

McFarlane also reported the chemical shifts of the C^{13} nuclei in $P(OCH_3)_3$ and $OP(OCH_3)_3$.[43] He determined that the C^{13} carbon in $P(OCH_3)_3$ is shielded by 6.0 ppm compared to $OP(OCH_3)_3$. This same difference in chemical shift was observed between $P(CH_3)_3$ and $SP(CH_3)_3$ or $SeP(CH_3)_3$, the C^{13} carbon in the trivalent phosphorus compound being more shielded. The C^{13} chemical shift of I (-37.88 ± 0.1 ppm) was observed to be 0.6 ppm to *lower* field than its dioxide (-37.28 ± 0.02 ppm) which contrasts with the results for the aforementioned compounds.

The factors governing the apparent preference of the metal carbonyls and the methyl carbonium ion for the PO_3 end of I under equilibrium conditions are not yet clear and need further study. The structure of I makes possible the investigation of some interesting metal coordination polymers of the linear, two-dimensional, and three-dimensional types. These studies are under way with transition metals in a variety of oxidation states.[44]

Acknowledgments. J. G. V. thanks the National Science Foundation for generous grant support of this research and grants which facilitated the purchase of the nmr and mass spectrometers. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

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(42) E. G. Finer and R. K. Harris, private communication.

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(44) NOTE ADDED IN PROOF. Quagliano and coworkers (V. L. Goedken, J. V. Quagliano, and L. M. Vallarino, *Inorg. Chem.*, 8, 2331 (1969); C. Ercolani, J. V. Quagliano, and L. M. Vallarino, *Chem. Commun.*, 1094 (1969); *Inorg. Chim. Acta*, **3**, 421 (1969)) have described complexes of the positively charged ligands $N(CH_2CH_2)_3{}^{+}NCH_3$ and $(C_6H_5)_2E(CH_2)_nE(C_6A_5)_2CH_2C_6H_5$ (where E = As, $n = 2$; E = P, $n = 1$ or 2). The ligating properties of the trivalent arsenic and phosphorus in the latter ligands are not detectably altered by the presence of a positive charge which is in agreement with our observations on $P(OCH_2)_3{}^{+}PCH_3$.