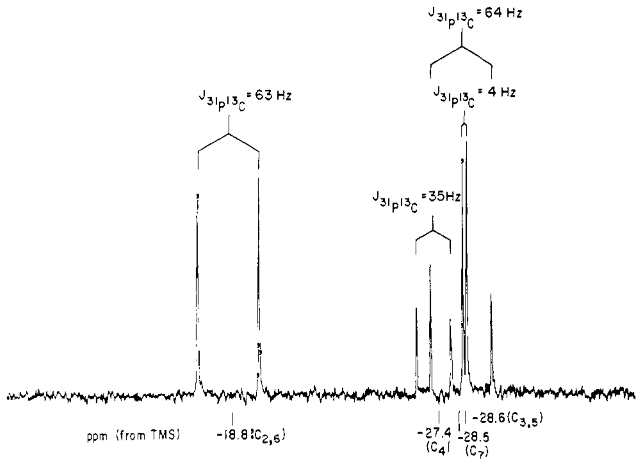
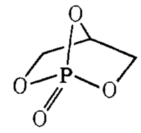


Figure 3. ^{13}C nmr spectrum of **1** ($CDCl_3$) determined at 24 kG under conditions of proton noise decoupling; scale, parts per million relative to carbons of tetramethylsilane.

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

The coupling constant ($J_{^{31}PCC^{1}H}$) of 28 Hz between phosphorus and the proton on the bridgehead carbon (C_4) is unusually large (*cf.* $J_{^{31}PCC^{1}H}$ for $(CH_3CH_2)_3P{=}O$ is 16.3 Hz).[24] Inspection of a molecular model shows that the dihedral angle between phosphorus and the coupled proton at C_4 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 $J_{^{31}PCC^{1}H}$ similar to the Karplus relationship for $J_{^{1}HCC^{1}H}$ values.[27] Also, White and Verkade[11] found an unusually large $J_{^{31}POC^{1}H}$ 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 C_7 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 $J_{^{31}PC^{13}C}$ coupling constant between the bridgehead atoms is an order of magnitude greater than the corresponding $J_{^{31}PC^{13}C}$ value between 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 C_7.[11,29] The nature of this effect is the subject of further investigation.

Acknowledgments. This work was supported by Petroleum Research Fund Grant No. 5738-AC4. We wish to thank T. I. Moder, P. L. Gendler, W. Horsley, D. T. Browne, and D. M. Wilson for various nmr measurements.

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[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 $J_{^{31}P^{13}C}$ values [G. J. Gray and S. E. Cremer, *J. Org. Chem.*, 37, 3458 (1972)].

[29] R. D. Bertrand, D. A. Allison, and J. G. Verkade, *J. Amer. Chem. Soc.*, **92**, 71 (1970).

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Received June 24, 1972

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

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 $(C_6H_5)_2PCH_2CH_2P^{+}(C_6H_5)_2CH_2C_6H_5[Br^{-}]$ and $(C_6H_5)_2PCH_2P^{+}(C_6H_5)_2CH_2C_6H_5[Br^{-}]$ 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 $(C_6H_5)_2P^{+}(CH_2)_2C(CH_3)CH_2P(C_6H_5)_2[Cl^{-}]$ 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 $P(OCH_2)_3P^{+}CH_3[BF_4^{-}]$.[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 $CoBr_3(P(C_6H_5)_2C{\equiv}CP^{+}(C_6H_5)_2CH_2C_6H_5)[Br^{-}]$.[5]

We have recently reported the preparation of complexes of the type $(OC)_5WP(C_6H_5)_2(CH_2)_yP(C_6H_5)_2$ and $(OC)_5WP(C_6H_5)_2(CH_2)_yP^{+}(C_6H_5)_2R[X^{-}]$ (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

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[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).

Table I. Phosphorus-31 Nmr Data[a]

Compound	$^1J_{W-P}$	$^3J_{W-P}$	δ_{W-P}	δ_P	J_{PP}
$(OC)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2$	240.0		−11.4	13.7	37.2
$(OC)_5WP(C_6H_5)_2CH_2CH_2P^+(C_6H_5)_2C_4H_9[PF_6^-]$	243.2		−15.2	−27.8	47.6
$(OC)_5WP(C_6H_5)_2CH_2P(C_6H_5)_2$	245.6	6.3	−10.0	24.8	106.2
$(OC)_5WP(C_6H_5)_2CH_2P^+(C_6H_5)_2CH_3[I^-]$	253.2		−5.44	−19.5	8.1

[a] Coupling constants are accurate to ±0.1 Hz. Chemical shifts are reported with respect to 85% H_3PO_4 with a positive value being taken as upfield from the acid. Phosphorus-31 nmr spectra were recorded with a Varian XL-100FT spectrometer.

position a small perturbation was observed. We present here a ^{31}P nmr study in which the magnitudes of tungsten-183–phosphorus-31 coupling constants have been measured for the quaternized and unquaternized complexes. These values provide the most quantitative evaluation yet reported of the effect of a positive charge on the metal–phosphorus bond.

The phosphorus-31 data are reported in Table I. The phosphorus-31 nmr spectra of $(OC)_5WP(C_6H_5)_2CH_2P(C_6H_5)_2$ and $(OC)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)$ confirm that only one phosphorus group in each complex is coordinated. The ^{31}P chemical shifts of the uncoordinated phosphorus atoms in these complexes are 24.8 and 13.7 ppm, respectively. These values are very similar to those which have been reported for $(C_6H_5)_2PCH_2P(C_6H_5)_2$ (22.8 ppm) and $(C_6H_5)_2CH_2CH_2P(C_6H_5)_2$ (12.5 ppm).[7] The relatively small changes in chemical shift which result from coordination suggest that changes in bond angles, electronegativities, and hyperconjugation are quite small for the phosphorus group which remains uncoordinated.[8] The spectra for both complexes show a large downfield shift relative to the free ligand for the coordinated phosphorus. The coordination chemical shifts for $(OC)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2$ and $(OC)_5WP(C_6H_5)_2CH_2P(C_6H_5)_2$ are −23.9 and −32.8 ppm, respectively. This is consistent with what has been reported for other systems.[9]

Further confirmation of the structure of these complexes is given by the observation of phosphorus–phosphorus coupling in each compound, which would be expected only if the two phosphorus nuclei are chemically nonequivalent. Finally, coupling of tungsten to phosphorus, consistent with that reported for complexes in which tungsten is bound directly to phosphorus, is found associated with the low-field resonance.

It has been established previously that the magnitudes of tungsten–phosphorus coupling constants, within a given series of compounds, increase as the electronegativities of the substituents attached to phosphorus increase.[9–11] The range of tungsten–phosphorus coupling constants heretofore reported is 227 ± 1 Hz [for $(OC)_5WP(C_4H_9)_3$][10] to 485 ± 5 Hz [for $(OC)_5WPF_3$].[11] For the series of complexes $(OC)_5WP(C_6H_5)(C_4H_9)_2$, $(OC)_5WP(C_6H_5)_2(C_4H_9)$, and $(OC)_5WP(C_6H_5)_3$, values of 235 ± 8, 250 ± 8, and 280 ± 8 Hz have been reported respectively.[8] The greater accuracy of our values (±0.1 Hz) prevents a precise comparison of our compounds to $(OC)_5WP(C_6H_5)(C_4H_9)_2$ and $(OC)_5WP(C_6H_5)_2C_4H_9$. From our data it would appear that the group, $-CH_2CH_2P^+(C_6H_5)_2C_4H_9$, is only slightly more electronegative than the group, $-CH_2CH_2P(C_6H_5)_2$, since J_{WP} for $(OC)_5WP(C_6H_5)_2CH_2CH_2P^+(C_6H_5)_2C_4H_9[Br^-]$ is 243.2 Hz, while for $(OC)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2$ it is 240.0 Hz. Differences in electron-withdrawing ability of $-CH_2P^+(C_6H_5)_2CH_3[I^-]$ and $-CH_2P(C_6H_5)_2$, however, are more pronounced, as shown by values of 245.6 Hz for $(OC)_5WP(C_6H_5)_2CH_2P(C_6H_5)_2$ and 253.2 Hz for $(OC)_5WP(C_6H_5)_2CH_2P^+(C_6H_5)_2CH_3[I^-]$. These results bear out our earlier findings.[6]

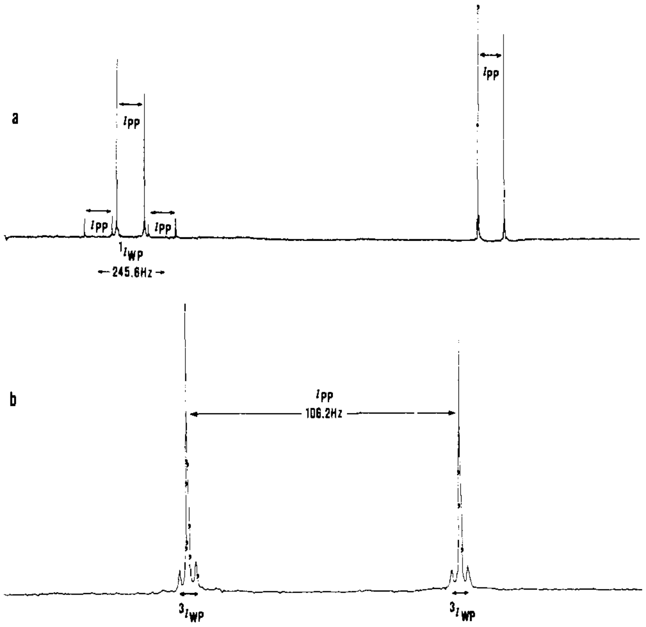

Figure 1. (a) Fourier transform ^{31}P nmr spectrum of $(OC)_5WP(C_6H_5)_2CH_2P(C_6H_5)_2$; (b) expanded ^{31}P nmr spectrum of the uncoordinated phosphine in $(OC)_5WP(C_6H_5)_2CH_2P(C_6H_5)_2$.

Of special significance is the observation of tungsten–phosphorus coupling (6.3 ± 0.1 Hz) through three bonds in the complex $(OC)_5WP(C_6H_5)_2CH_2P(C_6H_5)_2$ (Figure 1). This is the first reported observation of coupling between any heavy metal and phosphorus through more than one bond. Such coupling is not resolved for the quaternized complex. Upon quaternization, the angle about phosphorus increases such that it is nearly tetrahedral. This leads to greater s character in the phosphorus–methylene bond which might be expected to increase the value of the long-range coupling constant. If such an argument is valid, one would predict that $^3J_{WP}$ is negative and becomes approximately equal to zero when the complex is quaternized.

The absolute value of $^3J_{PP}$ (37.2 Hz) for $(OC)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2$ is smaller than for the quaternized complex ($^3J_{PP}$ = 47.6 Hz). The opposite is true for $(OC)_5WP(C_6H_5)_2CH_2P(C_6H_5)_2$ ($^2J_{PP}$ = 106.2

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(7) H. G. Horn and K. Sommer, *Spectrochim. Acta, Part A*, **27**, 1049 (1971).

(8) S. O. Grim, W. McFarlane, and E. F. Davidoff, *J. Org. Chem.*, **32**, 781 (1967).

(9) S. O. Grim, D. A. Wheatland, and W. McFarlane, *J. Amer. Chem. Soc.*, **89**, 5573 (1967).

(10) E. O. Fisher, L. Knauss, R. L. Keiter, and J. G. Verkade, *J. Organometal. Chem.*, **37**, c7 (1972).

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

Hz) and $(OC)_5WP(C_6H_5)_2CH_2P^+(C_6H_5)_2CH_3[I^-]$ ($^2J_{PP}$ = 8.1 Hz). For the ligand $P(OCH_2)_3P$, it has been observed that J_{PP} becomes more positive with increasing s character and effective nuclear charge.[4] If these patterns are followed in our systems, it would be predicted that $^3J_{PP}$ for $(OC)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)$ is positive and becomes more so upon quaternization, while $^2J_{PP}$ for $(OC)_5WP(C_6H_5)_2CH_2P(C_6H_5)_2$ is −106.2 Hz and becomes ±8.1 Hz upon quaternization. These predictions are based upon trends which have been observed for a relatively small number of systems and their validity will be established only by the determination of more signs of J_{PP}.[12]

Acknowledgment. Financial support from the Council of Faculty Research, Eastern Illinois University, is acknowledged.

(12) E. G. Finer and R. K. Harris, "Progress in NMR Spectroscopy," Vol. 6, Pergamon Press, Elmsford, N. Y., 1970, Chapter 2.

(13) (a) Eastern Illinois University; (b) Varian Associates.

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Synthesis with Zerovalent Nickel. Coupling of Alkenyl Halides with Bis(1,5-cyclooctadiene)nickel(0)

Sir:

Bis(1,5-cyclooctadiene)nickel(0)[1] is a powerful zerovalent nickel catalyst for diene oligomerization[2] and a reactive species in oxidative addition of allyl,[3] benzyl,[4] and aryl halides.[5] The study of the coupling of aryl halides with bis(1,5-cyclooctadiene)nickel [$Ni(COD)_2$] showed clearly that the nickel reagent reacts rapidly and selectively with certain carbon–halogen bonds in the presence of a wide variety of other functional groups.[5] Herein we report that alkenyl halides react in a parallel way with $Ni(COD)_2$, producing symmetrical 1,3-dienes directly. The mild reaction conditions and, in certain cases, the high efficiency and high stereospecificity of the process point to potential synthetic applications in inter- and intramolecular coupling of alkenyl halides.

The experimental procedure is illustrated for the conversion of *trans*-2-bromostyrene to *trans,trans*-1,4-diphenyl-1,3-butadiene. $Ni(COD)_2$ (563 mg; 2.08 mmol) was transferred to a three-necked flask which had been alternately evacuated and filled with argon three times, and 15 ml of oxygen-free dimethylformamide was added. With the mixture frozen at −78°, 683 mg (3.74 mmol) of *trans*-2-bromostyrene[6] was added all at once *via* syringe. The mixture was allowed to warm to 25° over 1 hr and then stirred at 25° for 10 hr followed by 35° for 2 hr. The mixture (homogeneous green) was poured into ether and washed with water several times. Quantitative ^1H nmr analysis and quantitative glpc analysis of the residue from the ether solution indicated the presence of *trans,trans*-1,4-diphenyl-1,3-butadiene in a yield of 70 ± 2%. Repeated crystallization from methyl alcohol gave colorless crystals (mp 149.5–151°, lit.[7] mp 153°) in 46% yield.

In the absence of electron-withdrawing groups, *i.e.*, with simple alkenyl halides, the yields of coupling products are only moderate, 34–60%, and a mixture of geometric isomers results, with an apparent tendency toward the more stable isomer (Table I). On the other hand, 2-halo- and 3-haloacrylates react very rapidly (−20 to 0°) with $Ni(COD)_2$ to produce symmetrical unsaturated diesters in high yield and with complete retention of configuration (Table II). The most important reason for the only moderate yields of the simple 1,3-dienes is likely to be catalytic oligomerization of the initially formed 1,3-diene by unreacted $Ni(COD)_2$ or a related intermediate nickel species;[2] in fact, longer reaction times (>24 hr/25°) lead to lower yields of coupling products.

The products reported in Tables I and II are known compounds with the exception of dibenzyl *trans,trans*-muconate (Table II, entry 7) which had mp 108–109° and showed spectral data in complete accord with the structure. For confirmation, the diester was hydrolyzed in aqueous base to afford *trans,trans*-muconic acid (mp 301°, lit.[8] mp 301°).

The isomeric 2,4-hexadienes (Table I) were collected separately by preparative glpc and identified by comparison of ir absorption maxima with those reported by Bartlett;[9] the isomers also showed the same order of elution observed by Whitesides, under the same glpc conditions.[10]

The coupling product from 2-bromo- and 2-chloroacrylates (Table II, entries 1–4), 2,3-dicarbomethoxy-1,3-butadiene, is easily polymerized and could not be isolated efficiently; the yields were determined using quantitative ^1H nmr analysis, by integration of the characteristic peaks due to the vinyl hydrogens in the product (δ 5.82 and 6.29) relative to a precise amount of an internal standard. Base hydrolysis of the crude mixture from the coupling reaction afforded 2,3-dicarboxy-1,3-butadiene, identical in ir absorption maxima with literature values;[11] mp 192–192.5°, lit.[11] 182–185°.

The ^1H nmr spectral data for the geometric isomers of dimethyl muconate clearly distinguish the isomers;[12] both the yields and identification of the products were done by analytical ^1H nmr spectroscopy for entries 5–7 in Table II. The task was simple because the reactions are stereospecific within the limits of ^1H nmr detection, estimated to be *ca.* 2%.

The reactions of the haloacrylate esters exemplify the mildness of the nickel-promoted coupling method.[13]

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(1) B. Bogdanovic, M. Kroner, and G. Wilke, *Justus Liebigs Ann. Chem.*, **699**, 1 (1966); for a detailed modified procedure for the preparation of bis(1,5-cyclooctadiene)nickel(0), see M. F. Semmelhack, *Org. React.*, **19**, 178 (1972).

(2) W. Brenner, P. Heimback, H. Hey, E. W. Muller, and G. Wilke, *Justus Liebigs Ann. Chem.*, **727**, 161 (1969), and references therein.

(3) (a) G. Wilke, *Angew. Chem., Int. Ed. Engl.*, **5**, 151 (1966); (b) M. F. Semmelhack, Ph.D. Thesis, Harvard University, 1967; (c) M. F. Semmelhack, *Org. React.*, **19**, 179 (1972).

(4) M. F. Semmelhack and P. M. Helquist, unpublished observations.

(5) M. F. Semmelhack, P. M. Helquist, and L. D. Jones, *J. Amer. Chem. Soc.*, **93**, 5908 (1971).

(6) E. Grovenstein, Jr., and D. E. Lee, *ibid.*, **75**, 2639 (1953).

(7) J. H. Pinkard, B. Wille, and L. Zechmeister, *ibid.*, **70**, 1938 (1948).

(8) J. A. Elvidge, *J. Chem. Soc.*, 2235 (1950).

(9) L. K. Montgomery, K. Schueller, and P. D. Bartlett, *J. Amer. Chem. Soc.*, **86**, 622 (1964).

(10) G. M. Whitesides, C. P. Casey, and J. M. Krieger, *ibid.*, **93**, 1379 (1971), and references cited therein.

(11) W. J. Bailey, R. L. Hudson, and E. T. Yates, *J. Org. Chem.*, **28**, 828 (1963).

(12) J. A. Elvidge and P. D. Ralph, *J. Chem. Soc. C*, 387 (1966).

(13) T. Cohen and T. Poeth, *J. Amer. Chem. Soc.*, **94**, 4363 (1972), and references cited therein.