Contribution from the Departments of Chemistry, Oakland University, Rochester, Michigan 48063,
and Eastern Illinois University, Charleston, Illinois 61920, and from Varian Associates, Palo Alto, California 94303

A Phosphorus-31 Nuclear Magnetic Resonance Study of Tungsten Carbonyl Complexes Containing Unsaturated Organophosphorus Cationic Ligands[1]

R. CRAIG TAYLOR,*[2] RICHARD L. KEITER,[3] and LEW W. CARY[4]

Received November 14, 1973 AIC30835H

The complexes $W(CO)_5L{-}L$ and $W(CO)_5L{-}L^+$, in which L–L represents cis or trans $(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$ and $(C_6H_5)_2PC{\equiv}CP(C_6H_5)_2$ and $L{-}L^+$ represents the monomethylated cations of these same three organophosphorus compounds, have been prepared and characterized with ^{31}P nmr, infrared, and mass spectra. Infrared frequencies and ^{31}P nmr spectra indicate that both L–L and $L{-}L^+$ are present in the complexes as monodentate ligands. Tungsten-183–phosphorus-31 coupling constants of the neutral and cationic complexes reveal that the presence of an unsaturated linkage between the donor and cationic sites as compared to the presence of a saturated linkage does not significantly facilitate the transmission of electronic charge. The relative changes in coupling constants ΔJ_{WP}, upon quaternization, increases in the series: $\Delta J_{(cis)} < \Delta J_{(-CH_2CH_2-)} < \Delta J_{(-C\equiv C-)} < \Delta J_{(trans)} < \Delta J_{(-CH_2-)}$. Phosphorus-31–phosphorus-31 coupling constants and ^{31}P chemical shifts also are discussed.

Introduction

The ligating properties of various cationic ligands have been compared previously with their nonprotonated and/or nonquaternized counterparts.[5-11] Cationic ligands $(L{-}L^+)$ such as $[(C_6H_5)_2P(CH_2)_yP^+(C_6H_5)_2R][X^-]$ in which $y = 1$ or 2, R = alkyl, and X = anion may form transition metal complexes which may be categorized as inorganic zwitterions of the type $[X_xM^-{\leftarrow}L{-}L^+]$ or as 1:1 electrolytes of the type $[Y_mM{\leftarrow}L{-}L^+][X^-]$.

Interest in complexes of both categories has centered primarily on various experimental attempts to assess the electronic influence of the positive charge on the metal–donor bond. The results of electronic and infrared spectral studies on the pseudotetrahedral zwitterions, $[X_3M^-{\leftarrow}L{-}L^+]$, in which M is a divalent first row transition metal ion and X = Cl, Br, and I, have shown that in all cases the positive charge associated with these ligands has little, if any, influence on the ligating properties of the donor atom.[6,8]

Infrared studies of some complexes of the type $[Y_mM{\leftarrow}L{-}L^+]X^-$, however, provide evidence for a positive charge influence upon the metal–phosphorus bond. A comparison of carbonyl stretching frequencies of $(OC)_5WP(C_6H_5)_2(CH_2)_yP(C_6H_5)_2$ and $[(OC)_5WP(C_6H_5)_2(CH_2)_yP^+(C_6H_5)_2R]X^-$ ($X = PF_6$, I) shows a measurable effect when $y = 1$ but no measurable effect when $y = 2$.[11] From ^{31}P nmr studies of the same complexes, it was found that $^1J_{WP}$ coupling constants increase upon quaternization of the noncoordinated phosphorus atom.[10] Furthermore, the increase was largest for the complex with $y = 1$.

Previously, it has been suggested that the influence of the positive charge might be more strongly felt in systems in which the cationic and donor sites are joined by an unsaturated organic skeleton rather than a saturated one.[6] To test that hypothesis we have carried out a ^{31}P nmr study of a series of tungsten carbonyl complexes in which the donor phosphine and the cationic site are separated by cis or trans ethylene or acetylene bridges.

Experimental Section

cis- and *trans*-1,2-bis(diphenylphosphino)ethylene were obtained from Pressure Chemical Co. and bis(diphenylphosphino)acetylene was obtained from Strem Chemicals. The preparations of the monoquaternized phosphonium salts of these ligands have been described previously.[6] The aniline complex, $(CO)_5WNH_2C_6H_5$, was prepared as described by Angelici and Malone.[12]

Phosphorus-31 nmr spectra were recorded with a Varian XL-100 spectrometer equipped with Fourier transform and a pulsed deuterium lock. The samples were examined in 12-mm tubes and 2.5 ml of $CDCl_3$ was used for solvent and lock. Phosphoric acid (85%) in a 1.0-mm capillary was suspended in the sample as an external reference. Coupling constants are accurate to ±0.1 Hz. Infrared spectra in the carbonyl region were recorded with a Perkin-Elmer 337 infrared spectrometer. These spectra were expanded with an E. H. Sargent SR recorder and are considered accurate to ± 2 cm^{-1}. Polystyrene was used as a frequency standard and chloroform was used as a solvent for each measurement. Mass spectra were recorded with a Du Pont 21-490 mass spectrometer at an energy of 70 eV and a source temperature of 240°. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn., and by Mr. Wilber Swanson, Department of Chemistry, University of Georgia, Athens, Georgia.

$(CO)_5W(cis\text{-}P(C_6H_5)_2CH{=}CHP(C_6H_5)_2)$ and $(CO)_5W[cis\text{-}P(C_6H_5)_2CH{=}CHP^+(C_6H_5)_2(CH_3)]I^-$. To a solution of *cis*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$ (0.8 g, 1.35 mmol) in benzene (50 ml) was added $(CO)_5WNH_2C_6H_5$ (0.962 g, 2.3 mmol). After 24 hr the solvent was removed with a rotary evaporator. The residue was eluted on a silica gel column with a solution of petroleum ether–ethyl acetate (2:1). The $(CO)_5WNH_2C_6H_5$ and $(CO)_5W[cis\text{-}P(C_6H_5)_2CH{=}CHP(C_6H_5)_2]$ came off together, followed by aniline. A fourth component did not come off and remained unidentified. The mixture of the starting carbonyl complex and the desired product was recrystallized with a dichloromethane–methanol mixture (1:1) to yield 0.90 g (93%) of $(CO)_5W[cis\text{-}P(C_6H_5)_2CH{=}CHP(C_6H_5)_2]$. The mass spectrum of the complex showed the expected parent ion pattern at a *m/e* 720. The melting point of the complex was 128.5–130.5°. This same complex was also prepared by the photolysis of $W(CO)_6$ in THF followed by the addition of the ligand. Freshly sublimed $W(CO)_6$ (1.0 g, 2.8 mmol) was dissolved in 150 ml of dry THF and the resultant solution was photolyzed for 4 hr with a mercury lamp. The lamp was turned off and a solution of *cis*-$P(C_6H_5)_2CH{=}CHP(C_6H_5)_2$ (1.0 g, 2.5 mmol) and CH_2Cl_2 (10 ml) was added. The mixture was flushed with dry nitrogen, stoppered, and stored in a refrigerator at −15° for 24 hr. The cold solution was filtered to remove a small amount of unreacted $W(CO)_6$

---

(1) Presented in part at the 165th National Meeting of the American Chemical Society, Dallas, Texas, April 1973; see Abstracts, No. INOR 155.

(2) Oakland University.

(3) Eastern Illinois University.

(4) Varian Associates.

(5) J. V. Quagliano, A. K. Banerjee, V. L. Goedken, and L. M. Vallarino, *J. Amer. Chem. Soc.*, 92, 482 (1970).

(6) R. C. Taylor and R. A. Kolodny, *Chem. Commun.*, 813 (1970); R. A. Kolodny, T. L. Morris, and R. C. Taylor, *J. Chem. Soc., Dalton Trans.*, 328 (1973).

(7) W. V. Dahlhoff, T. R. Dick, and S. M. Nelson, *J. Chem. Soc. A*, 2919 (1969).

(8) C. Ercolani, L. M. Vallarino, and J. V. Quagliano, *Inorg. Chim. Acta*, 3, 421 (1969).

(9) D. Berglund and D. W. Meek, *Inorg. Chem.*, 8, 2602 (1969).

(10) R. L. Keiter and L. W. Cary, *J. Amer. Chem. Soc.*, 94, 9232 (1972).

(11) R. L. Keiter and D. P. Shah, *Inorg. Chem.*, 11, 191 (1972).

(12) R. J. Angelici and M. D. Malone, *Inorg. Chem.*, 6, 1731 (1967).

and the filtrate was evaporated to dryness on a rotary evaporator. The crude product was dissolved in a minimum amount of CH_2Cl_2 and again filtered to remove a small quantity of $W(CO)_6$. Addition of methanol to the cold solution precipitated a pale yellow solid. An infrared spectrum of this solid indicated the presence of $(CO)_5W[$*cis*-$P(C_6H_5)_2CH{=}CHP(C_6H_5)_2]$ and some $W(CO)_6$. Residual traces of $W(CO)_6$ were vacuum sublimed at 45-50° (0.06 mm) from this material. An infrared spectrum of the nonsublimable material showed it to be free of $W(CO)_6$. A total of 0.48 g was obtained. An additional 0.38 g of product was isolated from the filtrate upon addition of more cold methanol. The over-all yield based on the ligand was 48%. A melting point of 128.5-130.5° was recorded. *Anal.* Calcd for $(CO)_5W[$*cis*-$P(C_6H_5)_2CH{=}CHP(C_6H_5)_2]$: C, 51.69; H, 3.08; P, 8.59. Found: C, 51.52; H, 3.17; P, 8.33.

This complex was methylated with methyl iodide in $CDCl_3$ to give $(CO)_5W[$*cis*-$P(C_6H_5)_2CH{=}CHP^+(C_6H_5)_2(CH_3)]I^-$ as verified by the ^{31}P nmr spectrum. The complex was not isolated.

$(CO)_5W[$*trans*-$P(C_6H_5)_2CH{=}CHP(C_6H_5)_2]$ and $(CO)_5W[$*trans*-$P(C_6H_5)_2CH{=}CHP^+(C_6H_5)_2(CH_3)]I^-$. A 100-ml solution containing $(CO)_5WNH_2C_6H_5$ (1.0 g, 1.7 mmol) and *trans*-$P(C_6H_5)_2CH{=}CHP(C_6H_5)_2$ (2.0 g, 5.0 mmol) was allowed to stand for 24 hr. The solvent was removed from the reaction mixture and the product was recrystallized with a CH_2Cl_2-CH_3OH solution (1:1). Crystals slowly formed and over a period of several days four fractions were collected. The second fraction contained 0.75 g of pure $(CO)_5W[$*trans*-$P(C_6H_5)_2CH{=}CHP(C_6H_5)_2]$. The complex melted at 131-133°.

A solution of $(CO)_5W[$*trans*-$P(C_6H_5)_2CH{=}CHP(C_6H_5)_2]$ (0.25 g) in 30 ml of benzene was treated with excess CH_3I. Crystals formed over a period of 48 hr and they were shown by ^{31}P nmr to be $(CO)_5W[$*trans*-$P(C_6H_5)_2CH{=}CHP^+(C_6H_5)_2(CH_3)]I^-$. The crystals decomposed over the temperature range of 150-157°.

$(CO)_5W[P(C_6H_5)_2C{\equiv}CP(C_6H_5)_2]$ and $(CO)_5W[P(C_6H_5)_2C{\equiv}CP^+(C_6H_5)_2(CH_3)]I^-$. The unquaternized complex was prepared by the procedure used for the trans complex. Recrystallization of the impure $(CO)_5W[P(C_6H_5)_2CCP(C_6H_5)_2]$ gave the pure compound in the third fraction. A parent ion centered at 718 was found in the mass spectra. The complex melted at 75-77°.

The quaternized complex was not isolated but was formed when CH_3I was added to a $CDCl_3$ solution of $(CO)_5W[P(C_6H_5)_2CCP(C_6H_5)_2]$. This result was confirmed by the ^{31}P nmr spectrum.

Results and Discussion

The neutral tungsten pentacarbonyl phosphine complexes, $(CO)_5W{\leftarrow}L{-}L$, in which L-L represents one of the three unsaturated organophosphorus ligands studied in this work, were isolated in good yields by displacing aniline from $(CO)_5WNH_2C_6H_5$.[11,13] These reactions proceed smoothly at room temperature thereby minimizing thermal decomposition. The stoichiometric ratio of reactants to products varied depending on the particular phosphine chosen because of the possible formation of the dimetallic complex, $(OC)_5WL{-}LW(CO)_5$. From examination of a molecular model of $[(CO)_5W$-*cis*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2]$ it was concluded that a dimetallic complex was not sterically possible; hence a molar excess of $(CO)_5WNH_2C_6H_5$ was used. Column chromatography on silica gel of the crude reaction mixture afforded starting material, aniline, and the desired 1:1 complex in excellent yield. It was also possible to prepare the same complex, albeit in much poorer yield, by photolyzing $W(CO)_6$ in THF, followed by addition of the ligand. In order to minimize the formation of the dimetallic complexes for the other two ligands it was necessary to employ a 3:1 molar ratio of ligand to $(CO)_5WNH_2C_6H_5$.

The complexes containing the positively charged ligands were obtained by allowing the neutral complexes to react with methyl iodide. Only in the case of $[(CO)_5W$-*trans*-$(C_6H_5)_2PCH{=}CHP^+(C_6H_5)_2CH_3]I^-$ was the cationic complex actually isolated. The corresponding cationic complexes of the other two ligands were prepared *in situ* by adding a stoichiometric amount of CH_3I directly to a $CDCl_3$ solution of the neutral complex in the nmr tube. Formation of the desired cationic complexes was verified by the ^{31}P nmr spectra (*vide infra*).

Mass Spectra. Each of the neutral complexes exhibited a molecular ion peak in the mass spectrum. The observation of the parent ion is interesting in view of the recently published results of Connor, *et al.*[14] These investigators studied the mass spectra of complexes of formulation $(CO)_5WL$, in which M = Cr, Mo, and W and L = $(CH_3)_2PC_2H_4P(CH_3)_2$, $(C_6H_5)_2PCH_2P(C_6H_5)_2$, $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$, $(C_6H_5)_2PC_3H_6P(C_6H_5)_2$, and $(C_6H_5)_2PC_2H_4As(C_6H_5)_2$, and observed that none of these complexes exhibited a parent ion. They attributed the failure to observe $(CO)_5WL^+$ as indicative of the rapid conversion of $(CO)_5WL$ into $(CO)_4WL$ brought about by a combination of the high source temperature (50-70°) and the energy of the electron beam (70 eV). This result is not too surprising considering the flexibility of the ligands and the ease with which chelation can take place. In the present study the observation of a parent ion for $[(CO)_5W$-*cis*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2]$ is therefore somewhat surprising in view of the conformation of the ligand. In fact, during the preparation of the complex, care had to be exercised (avoidance of elevated temperature) in order to prevent the formation of the tetracarbonyl species. This fact together with the higher source temperature employed (240°) would tend to favor formation of $[(CO)_4W$-*cis*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2]$. The appearance of the $(CO)_5WL^+$ ion for this complex must reflect some inherent stability for this species which is not present in the saturated complex.

It is obvious that the trans and acetylene ligands, for steric reasons, cannot serve as chelates. However, it was noted during the syntheses of the complexes containing these ligands that they have a tendency to form dimetallic species. The dimetallic parent ion was not observed in the mass spectrum of either of these complexes. It is reasonable to assume that the failure to observe these species may be attributed to the rapid loss of CO at the source temperature employed.

In addition to the molecular ions, the cis and trans complexes exhibited ion fragments which were attributed to the stepwise loss of CO. The acetylene complex did not exhibit a $(CO)_4WL^+$ ion.

Infrared Spectra. In the region 2200-1800 cm^{-1}, the neutral and cationic complexes showed the pattern of absorption bands expected for complexes of pseudo-C_{4v} symmetry.[15] The frequencies of the carbonyl stretching vibrations in $CHCl_3$ are listed in Table I. The spectra were characterized by the $A_1^{(1)}$, $A_1^{(2)}$, and E modes expected for local C_{4v} symmetry. The $A_1^{(1)}$ and E modes were not resolvable either because of accidental degeneracy or because of the width of the absorption bands. The forbidden B_1 mode was observed in all cases.

It is apparent from the data in Table I that stretching frequencies do not vary appreciably among the neutral and cationic complexes. Within experimental error it has been shown previously that the carbonyl infrared spectra of $(OC)_5W[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]$ and $(OC)_5W[(C_6H_5)_2PCH_2CH_2P^+(C_6H_5)_2CH_2C_6H_5)][PF_6^-]$, of $(OC)_5WP(OCH_2)_3P$ and $[(OC)_5WP(OCH_2)_3P^+CH_3][BF_4^-]$, and of $(OC)_5Cr(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ and $[(OC)_5Cr(C_6H_5)_2PCH_2CH_2P^+(C_6$-

---

[13] S. O. Grim, J. Del Gaudio, C. A. Tolman, and J. P. Jesson, *Inorg. Nucl. Chem. Lett.*, 9, 1083 (1973).

[14] J. A. Connor, J. P. Day, E. M. Jones, and G. K. McEwen, *J. Chem. Soc., Dalton Trans.*, 347 (1973).

[15] F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, 84, 4432 (1962); C. S. Kraihanzel and F. A. Cotton, *Inorg. Chem.*, 2, 533 (1963).

Table I. Infrared Carbonyl Stretching Frequencies for Monosubstituted Tungsten Pentacarbonyl Complexes[a]

Complex	Freq, cm^{-1}		
	$A_1^{(2)}$	B_1	$E, A_1^{(1)}$
$(CO)_5W[\textit{cis}-(C_6H_5)_2PCH=CHP(C_6H_5)_2]$	2073	1983	1944
$(CO)_5W[\textit{trans}-(C_6H_5)_2PCH=CHP(C_6H_5)_2]$	2074	1983	1940
$(CO)_5W[\textit{trans}-(C_6H_5)_2PCH=CHP^+(C_6H_5)_2CH_3]I^-$	2075	1989	1939
$(CO)_5W[(C_6H_5)_2PC\equiv CP(C_6H_5)_2]$	2076	1987	1939
$(CO)_5W[(C_6H_5)_2PC\equiv CP^+(C_6H_5)_2CH_3]I^-$	2077	1988	1946
$(OC)_5W[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]$[b]	2074	1986	1940
$(OC)_5W[(C_6H_5)_2PCH_2CH_2P^+(C_6H_5)_2CH_2C_6H_5)][PF_6^-]$[b]	2076	1990	1938
$(OC)_5W[(C_6H_5)_2PCH_2P(C_6H_5)_2$[b]	2072	1981	1939
$(OC)_5W[(C_6H_5)_2PCH_2P^+(C_6H_5)_2CH_3]I^-$[b]	2078	1989	1952, 1938
$(OC)_5WP(OCH_2)_3P$[c]	2085		1901, 1948
$[(OC)_5WP(OCH_2)_3P^+CH_3][BF_4]^-$[c]	2085		1912, 1947

[a] Complexes run in $CHCl_3$. All spectra calibrated with polystyrene. Frequencies are believed accurate to ±2 cm^{-1}. [b] Reference 11. [c] Reference 16.

Table II. ^{31}P Nmr Data for the Neutral and Cationic Ligands[a]

Ligand	Solvent[b]	δ_P	δ_{P^+}	$\lvert{}^3J_{PP^+}\rvert$
$\textit{cis}-(C_6H_5)_2PCH=CHP(C_6H_5)_2$	CH_3OH	+22.8		
$[\textit{cis}-(C_6H_5)_2PCH=CHP^+(C_6H_5)_2CH_2C_6H_5]Br^-$	CH_3OH	+26.0	−12.6	
	$CDCl_3$	+24.75	−13.81	18.7
$\textit{trans}-(C_6H_5)_2PCH=CHP(C_6H_5)_2$	CH_3OH	+7.7		
$[\textit{trans}-(C_6H_5)_2PCH=CHP^+(C_6H_5)_2CH_2C_6H_5]Br^-$	CH_3OH	−0.3	−17.5	
	$CDCl_3$	+1.5	−18.3	7.0
$(C_6H_5)_2PC\equiv CP(C_6H_5)_2$	CH_3OH	+32.0		
$[(C_6H_5)_2PC\equiv CP^+(C_6H_5)_2CH_2C_6H_5]Br^-$	CH_3OH	+32.2	−10.2	
	$CDCl_3$	+31.84	−11.67	6.8

[a] Solvent indicated, with 85% H_3PO_4 as external reference. [b] Data in CH_3OH taken from ref 6. Data in $CDCl_3$, this work.

Table III. ^{31}P Nmr Data for the Monosubstituted Tungsten Pentacarbonyl Complexes[a]

Complex	$\lvert{}^1J_{WP}\rvert$, Hz	$\lvert{}^3J_{PP}\rvert$, Hz	δ_{WP}	δ_P	Δ_{WP}[b]	Δ_P[b]
$(CO)_5W[\textit{cis}-(C_6H_5)_2PCH=CHP(C_6H_5)_2]$	238.3	37.2	−4.90	+28.68	−27.7	+5.9
$(CO)_5W[\textit{cis}-(C_6H_5)_2PCH=CHP^+(C_6H_5)_2CH_3]I^-$	238.2	11.2	−11.69	−10.43	−36.4	+3.4
$(CO)_5W[\textit{trans}-(C_6H_5)_2PCH=CHP(C_6H_5)_2]$	239.7	9.5	−13.08	+6.35	−20.8	−1.5
$(CO)_5W[\textit{trans}-(C_6H_5)_2PCH=CHP^+(C_6H_5)_2CH_3]I^-$[c]	245.1	34.5	−20.25	−18.79	−21.8	−.5
$(CO)_5W[(C_6H_5)_2PC\equiv CP(C_6H_5)_2]$	245.0	5.6	+6.64	+32.21	−25.4	+.2
$(CO)_5W[(C_6H_5)_2PC\equiv CP^+(C_6H_5)_2CH_3]I^-$	249.3	2.2	−2.55	−7.67	−34.4	+4.0
$(CO)_5W[(C_6H_5)_2PC_2H_4P(C_6H_5)_2]$[d]	240.0	37.2	−11.4	+13.7	−23.9	+1.2
$(CO)_5W[(C_6H_5)_2PC_2H_4P^+(C_6H_5)_2C_4H_9]PF_6^-$[d]	243.2	47.6	−15.2	−27.8		
$(CO)_5W[(C_6H_5)_2PCH_2P(C_6H_5)_2]$[d]	245.6	106.2	−10.0	+24.8	−32.8	−2.0
$(CO)_5W[(C_6H_5)_2PCH_2P^+(C_6H_5)_2CH_3]I^-$[d]	253.2	8.1	−5.44	−19.5		

[a] For $CDCl_3$ solution with 85% H_3PO_4 as external reference. [b] See text. [c] The chemical shift for this complex forms an AB pattern (see Figure 1). [d] From ref 10.

$H_5)_2CH_3][BF_4^-]$ are superimposable.[11,14,16] In this study the same invariance is noted for the complexes $(OC)_5W[\textit{trans}-(C_6H_5)_2PCH=CHP(C_6H_5)_2]$ and $(OC)_5W[\textit{trans}-(C_6H_5)_2PCH=CHP^+(C_6H_5)_2CH_3]I^-$ if one takes into consideration that the B_1 mode is weak and broad and therefore not well defined. Small changes in carbonyl stretching frequencies are noted for the complexes $(OC)_5W[(C_6H_5)_2PC\equiv CP(C_6H_5)_2]$ and $[(OC)_5W(C_6H_5)_2PC\equiv CP^+(C_6H_5)_2CH_3]I^-$ and the previously reported pair[11] $(OC)_5W[(C_6H_5)_2PCH_2P(C_6H_5)_2$ and $(OC)_5W[(C_6H_5)_2P^+CH_2P(C_6H_5)_2CH_3]I^-$. The small increases in carbonyl stretching frequencies upon quaternization are consistent with an expected increase in electron withdrawing power of the phosphorus substituent. One could conclude that the $-C\equiv C-$ bridge is slightly better at transmitting electronic information that the $-CH_2CH_2-$bridge. However, care should be exercised in making deductions about the relative influence of the positive charge on the π-acceptor σ-donor properties of these ligands based solely on these data.

^{31}P Nmr Spectra. The phosphorus-31 nmr spectral data for the ligands and complexes prepared in this study are listed in Tables II and III, respectively. These data conclusively verify the nature of the phosphorus atoms in these complexes. In the neutral complexes the potentially bidentate phosphine ligands are coordinated to the tungsten atom through only one of the phosphorus atoms. Furthermore, rapid intramolecular exchange of the two phosphorus atoms is not occurring. Thus two separate phosphorus resonances are observed, one at a chemical shift value in the region where the resonance occurs for the uncomplexed ligand the other at a much lower field which has been assigned to the coordinated phosphorus atom. This large downfield ^{31}P chemical shift upon coordination is typical for phosphine complexes of tungsten. The low-field resonance occurs at a 1:11.5:1 system of equally spaced peaks which results from the coupling of 100% abundant ^{31}P with 14.83% abundant ^{183}W. Further splitting of this 1:11.5:1 system and the splitting of the upfield ^{31}P resonance is caused by phosphorus-phosphorus coupling over three bonds, $^3J_{PP}$.

Examination of the ^{31}P spectrum for each of the cationic complexes shows two resonances at much lower fields relative to the chemical shift for the free ligands. Based on the appearance of the ^{183}W-^{31}P satellites it has been possible to

---

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

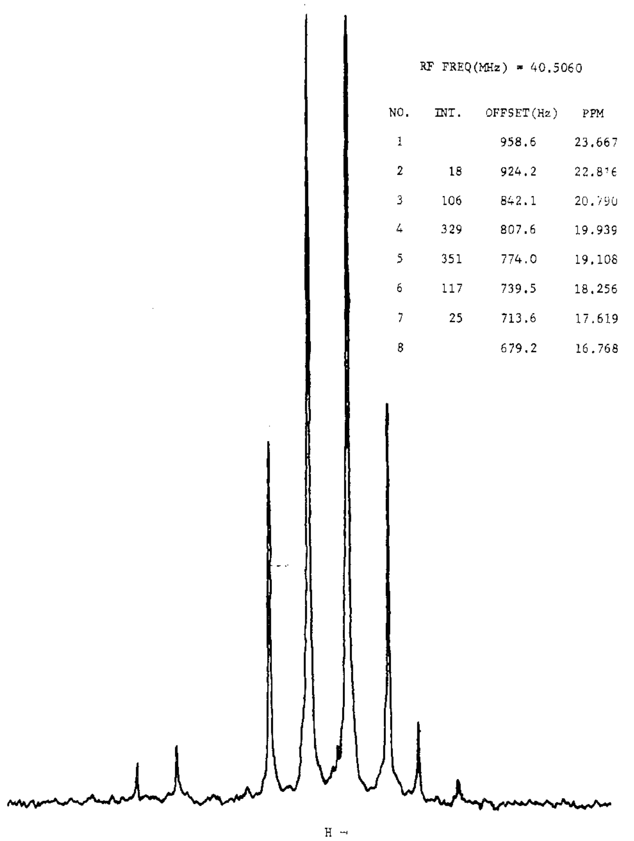
make an unequivocal assignment for the coordinated and quaternized phosphorus atoms. Even in the case of the trans cationic complex, which exhibits an AB pattern (see Figure 1) the correct assignment for δ_{WP} and δ_{P^+} was quite straightforward.

The data from a previous study have also been included in Table III for purposes of comparison and the discussion that follows. These data provide quantitative information concerning the influence of a cationic charge on the tungsten-phosphorus bond in both saturated and unsaturated organophosphorus ligands. The two experimental observables which were obtained from the ^{31}P nmr spectra are the absolute magnitudes of the ^{183}W-^{31}P and ^{31}P-^{31}P coupling constants, $|^1J_{WP}|$ and $|^3J_{PP}|$, and the ^{31}P chemical shifts. Each of these terms will be considered in turn.

(a) Coupling Constants. The magnitudes of the nuclear spin-spin coupling constants for ^{31}P coupled to various transition metal ions have been measured and discussed by numerous groups.[17] These measurements have been made in order to gain further insight into the nature of the metal-phosphorus bond.

McFarlane and Rycroft have established that the sign of $^1J(^{31}P-^{183}W)$ in $[(CH_3)_2(C_6H_5)P]W(CO)_5$ is positive, and trends in the magnitudes of coupling constants found in other $LW(CO)_5$ complexes indicate strongly that this is always true.[18] It seems apparent, therefore, that the Fermi contact mechanism is dominant in these coupling interactions. Thus variations in coupling constants arise principally from changes in effective nuclear charge and s character of the hybrid orbitals used by phosphorus. It is well established that ^{183}W-^{31}P coupling constants increase as the electronegativities of the substituents on phosphorus increase.[19,20] This would be expected since s character tends to concentrate in the bond formed with the most electropositive substituent.[21] Further, as the electronegativities of the substituents on phosphorus increase, phosphorus becomes more positive which should lead to a larger coupling constant.[22] Discussion still continues as to whether or not the s electron density is significantly enhanced by a synergic mechanism involving π-electron accepting capability of the trivalent phosphorus ligand.[23-25]

The electronegativities of the unsaturated organic moieties attached to phosphorus in the complexes of this study are nearly identical based on the data presented by Wilmshurst.[26] The group electronegativities for $CH{=}CH_2$, $C{\equiv}CH$, $C{\equiv}CCl$, and $C{\equiv}N$ are 3.12, 3.15, 3.11, and 3.11, respectively. Although the actual electronegativity values for the organophosphines are not known, it is apparent from the above data that a substituent on the β carbon in either the ethylene or acetylene series has little effect on the over-all group electronegativity. As a result, the ^{183}W-^{31}P coupling constants in the neutral complexes for the series of unsaturated organophosphines are similar (Table III). Even inclusion of the coupling constants for the neutral complexes containing the saturated bridges does not alter the observed range. Quaternization of the noncoordinated phosphorus atom should increase the electronegativity of the substituent and, as predicted by the arguments presented above, should cause an increase in the coupling constant. Such is the case, although the changes are small. The relative changes in coupling constants, ΔJ, upon quaternization are $\Delta J_{(CH_2)} > \Delta J_{(\text{trans})} > \Delta J_{(\text{acetylene})} > \Delta J_{(C_2H_4)} > \Delta J_{(\text{cis})}$. The absolute magnitudes for ΔJ_{WP} range from 7.6 to 0 Hz.



```
RF FREQ(MHz) = 40.5060

NO.   INT.   OFFSET(Hz)   PPM
 1             958.6     23.667
 2     18      924.2     22.816
 3    106      842.1     20.790
 4    329      807.6     19.939
 5    351      774.0     19.108
 6    117      739.5     18.256
 7     25      713.6     17.619
 8             679.2     16.768
```

Figure 1. AB pattern for $W(CO)_5[\textit{trans}\text{-}(C_6H_5)_2PCH{=}CHP^+(C_6H_5)_2CH_3]I^-$. Chemical shift data listed in the insert are measured from left to right and are downfield from 85% H_3PO_4. Computed coupling constants and chemical shifts are listed in Table III. Intensity data for peaks 1 and 8 were missing from the original computer readout.

It appears that electronic information is transmitted very poorly through the olefin linkage since ΔJ_{WP} is zero. It also appears that the transmittance of electronic information is more effective through the trans olefin linkage than the acetylene one and both lead to more effective transmittance than through the saturated bridge, $-CH_2CH_2-$. In no case is the presence of an unsaturated linkage between the donor and cationic sites as effective as the presence of a positive charge in a position α to the bonding phosphorus atom. It should be noted that the over-all range of coupling constants in the series of complexes, both neutral and cationic, presented in Table III is only 15 Hz. The midrange value for the series (245 Hz) is very close to that observed for $C_4H_9(C_6H_5)_2PW(CO)_5$ (250 Hz).[24]

It also has been possible to measure the absolute magnitudes of the ^{31}P-^{31}P coupling constants, $^3|J_{PP}|$, for the quaternized ligands as well as the tungsten complexes. It is apparent that these coupling interactions are very dependent upon the dihedral angles as well as electronic distribu-

---

(17) J. F. Nixon and A. Pidcock, *Annu. Rev. NMR (Nucl. Magn. Resonance) Spectrosc.*, 2, 345 (1969), and references cited therein.

(18) W. McFarlane and D. S. Rycroft, *J. Chem. Soc., Chem. Commun.*, 336 (1973).

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

(20) E. O. Fischer, L. Knauss, R. L. Keiter, and J. G. Verkade, *J. Organometal. Chem.*, 37, C7 (1972).

(21) H. A. Bent, *Chem. Rev.*, 61, 275 (1961).

(22) D. M. Grant and W. M. Letcher, *J. Amer. Chem. Soc.*, 87, 3994 (1965).

(23) S. O. Grim, R. L. Keiter, and W. McFarlane, *Inorg. Chem.*, 6, 1133 (1967).

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

(25) S. O. Grim, H. J. Plastas, C. L. Huheey, and J. E. Huheey, *Phosphorus*, 1, 61 (1971).

(26) J. K. Wilmshurst, *J. Chem. Phys.*, 27, 1129 (1957).

tion. The absolute values for $^3J_{PP}$ for the cis, acetylene and CH_2 neutral complexes are larger than for the quaternized species. The opposite is true for the trans and C_2H_4 neutral and cationic complexes. It has been found previously that $^3J_{PP}$ for the ligand $P(OCH_2)_3P$ becomes larger with increasing s character and effective nuclear charge suggesting the dominance of the Fermi contact term.[16] One cannot account for the magnitudes of $^3|J_{PP}|$ in this study with simple qualitative arguments. The signs of the coupling constants appear to vary from compound to compound.

(b) Chemical Shifts. It has been convenient to define a coordination chemical shift, Δ, as $\Delta = \delta$ complex $- \delta$ free ligand.[23] This value is invariably negative for group VI metal carbonyl derivatives, and for monodentate tertiary phosphine complexes, $LW(CO)_5$, it is approximately -20.[24] The Δ values we observe for phosphorus bonded to tungsten range from -20.8 for *trans*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$ to -36.4 for [*cis*-$(C_6H_5)_2PCH{=}CHP^+(C_6H_5)_2CH_3]I^-$. Δ values for uncoordinated phosphorus range from -0.5 to $+5.9$ showing that the shift may be in either direction.

The isotropic paramagnetic term is considered to be the most important contributor to ^{31}P chemical shifts.[27,28] This term depends on occupancy of phosphorus d orbitals, electronegativity of the substituents on phosphorus, changes in bond angles at phosphorus, and inversely on the mean excitation energy. It is of interest to compare the chemical shifts of the cis and trans complexes. The chemical shift difference for the neutral complexes is 8.18 and for the charged complexes it is 8.56. Electronegativity arguments fail to account for the difference since the two ligands should have identical group electronegativities. Although bond angles at the phosphorus atom in these complexes are not known from any definitive structural information, the change in phosphorus bond angle upon coordination should be quite similar for both ligands. Therefore, it is likely that d-orbital occupancy plays an important part in determining the ^{31}P chemical shifts of the unsaturated ligands.

X-Ray crystallographic data[29] for $(C_6H_5)_2PC{\equiv}CP(C_6H_5)_2$ indicate that the short P–C≡ bond length (1.765 Å) is probably due to appreciable dπ–pπ bonding between an appropriate d orbital on phosphorus and the pπ orbital of the acetylenic linkage. Substantial dπ–pπ bonding between phosphorus and carbon has also been cited as support for an abnormally low C≡C stretching frequency in the Raman spectra of diphosphino acetylenes. Whereas normal C≡C stretching frequencies occur in the region around 2300–2175 cm^{-1},[30] the C≡C frequency occurs at 2097 cm^{-1} in the solid state Raman spectrum of $(C_6H_5)_2PC{\equiv}CP(C_6H_5)_2$.[31] These latter authors have attributed the low stretching frequency to a drift of bonding π-electron density from the acetylene bond to the empty dπ orbital on phosphorus. The nearly linear PC≡CP framework[29] would facilitate this process. Finally, the ^1H nmr of numerous ethynyl phosphines is indicative of the presence of 3d orbital participation in the P–C≡C bond.[32] Presumably the same arguments apply, albeit not in the same quantitative sense, to the *cis*- and *trans*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$.

Applying these considerations to the present study, it seems appropriate to attribute the differences in chemical coordination shifts to changes in the d-orbital occupancy on the phosphorus atoms caused by changes both in the dπ–dπ overlap with the tungsten atom and in the dπ–pπ overlap with the acetylenic and ethylenic linkages. That the chemical shift differences between neutral and cationic complexes are greatest for the complexes containing the unsaturated ligands and least for the saturated ligands suggests appreciable dπ–pπ interaction is likely in the former species. Although the above arguments are somewhat speculative, the mechanism for the different ^{31}P chemical shifts is probably based on a synergic effect involving subtle changes in the σ-donating and π-accepting capacities for these ligands.

Acknowledgment. Partial support of this work by the Eastern Illinois University Research Council is gratefully acknowledged.

Registry No. $(CO)_5W$[*cis*-$[C_6H_5)_2PCH{=}CHP(C_6H_5)_2]$, 51472-39-0; $(CO)_5W$[*cis*-$(C_6H_5)_2PCH{=}CHP^+(C_6H_5)_2CH_3]I^-$, 51540-04-6; $(CO)_5W[($*trans*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2]$, 51540-05-7; $(CO)_5W$-[*trans*-$(C_6H_5)_2PCH{=}CHP^+(C_6H_5)_2CH_3]I^-$, 51540-06-8; $(CO)_5W$-$[(C_6H_5)_2PC{\equiv}CP(C_6H_5)_2]$, 51540-07-9; $(CO)_5W[(C_6H_5)_2PC{\equiv}CP^+$-$(C_6H_5)_2CH_3]I^-$, 51540-08-0; $(CO)_5WNH_2C_6H_5$, 16969-72-5; P, 7723-14-0.

---

(27) K. J. Packer, *J. Chem. Soc., London*, 960 (1963).

(28) H. S. Gutowsky and J. Larmann, *J. Amer. Chem. Soc.*, **87**, 3815 (1965).

(29) J. C. J. Bart, *Acta Crystallogr., Sect. B*, **25**, 489 (1969).

(30) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, San Francisco, Calif., 1962.

(31) A. J. Carty and A. Efraty, *Chem. Commun.*, 1559 (1968).

(32) W. Drenth and D. Rosenberg, *Recl. Trav. Chem. Pays-Bas*, **86**, 26 (1967); D. Rosenberg and W. Drenth, *Tetrahedron*, **27**, 3893 (1971).