

solidified on cooling to give 26 g (96%) of solid which was purified by recrystallization from methanol; mp 91–92°. This material may also be distilled *in vacuo*, bp 158° (1.5 mm). *Anal.* Calcd for $C_{14}H_{26}B_2N_4$: C, 61.8; H, 9.56; N, 20.6. Found: C, 62.5; H, 9.22; N, 20.7.

The infrared spectrum contained the BH_2 band as a complex multiplet in the 2270–2450- cm^{-1} range.

The nmr spectrum is confirmatory: it has singlets at τ 4.14, 7.66, and 7.78 as well as a complex multiplet (B-ethyls) at τ 9.1–9.8 in the correct 1:3:3:5 ratio.

The ultraviolet spectrum has λ_{max} 219 $m\mu$ (ϵ 17,800).

4,4-Diethyl-8,8-bis(1-pyrazolyl)pyrazabole.—To a mechanically stirred slurry of 16 g (0.05 mol) of potassium tetrakis(1-pyrazolyl)borate in 200 ml of toluene was added 42 ml of a 1.7 *M* solution of diethylboryl methanesulfonate in toluene. The slurry was stirred and refluxed for 1 hr. It was then cooled, stirred with water, and extracted with ether. The organic layer was dried, filtered, and evaporated, and the residue was chromatographed on acid-washed alumina eluting first with hexane (which removed some 4,4,8,8-tetraethylpyrazabole) and then with ether which eluted the desired product. It was obtained in 12.7-g (73%) yield and was purified further by recrystallization from heptane; mp 120–121°. *Anal.* Calcd for $C_{16}H_{22}B_2N_8$: C, 55.2; H, 6.32; N, 32.2. Found: C, 55.3; H, 6.45; N, 32.8.

The nmr spectrum is confirmatory: it has two overlapping doublets at τ 2.26, a doublet ($J = 2.6$, $J' = 0.7$ cps) at τ 2.54, a doublet ($J = 2.3$, $J' = 0.6$ cps) at τ 3.05, a triplet ($J = 2.5$ cps) at τ 3.48, a "triplet" (overlapping doublets $J = 2.3$ and 1.7 cps) at τ 3.74, and an asymmetric "doublet" (B-ethyls) at τ 9.48 in the correct 2:1:1:1:1:5 ratio.

The ultraviolet spectrum has λ_{max} 218 $m\mu$ (ϵ 19,400).

4,4-Dichloro-8,8-diethylpyrazabole.—Chlorine was bubbled into a solution of 43.2 g (0.2 mol) of 4,4-diethylpyrazabole in 500 ml of carbon tetrachloride until the yellow color persisted. The solution was evaporated to dryness and the residue was recrystallized from hexane. The product was obtained in 51.5-g (90.5%) yield as colorless crystals, mp 90–91°. *Anal.* Calcd for $C_{10}H_{16}B_2Cl_2N_4$: C, 42.1; H, 5.62; Cl, 24.9; N, 19.7. Found: C, 41.5; H, 5.30; Cl, 24.4; N, 19.7.

The nmr spectrum has doublets at τ 1.76 ($J = 2.5$ cps) and τ 2.25 ($J = 2.3$ cps), a triplet at τ 3.37 ($J = 2.4$ cps), and a multiplet at about τ 9.4 in 1:1:1:5 ratio.

4,4-Diethyl-8,8-phenylenedioxyppyrzabole.—A mixture of 10.8 g (0.05 mol) of 4,4-diethylpyrazabole and 5.5 g (0.05 mol) of pyrocatechol was refluxed in 150 ml of xylene. Hydrogen evolution was sluggish. The solvent was distilled out, whereupon hydrogen evolution speeded up and soon 2.4 l. was collected. The crude reaction mixture was chromatographed on alumina. Eluting with hexane gave 1.7 g of a solid which was identified as 4,4-diethylpyrazabole. Switching to ether-hexane as eluent produced a second fraction in 11.8-g yield (79% based on unrecovered 4,4-diethylpyrazabole). The material was recrystallized from heptane; mp 82–83°. *Anal.* Calcd for $C_{16}H_{20}B_2N_4O_2$: C, 59.6; H, 6.22; N, 17.4. Found: C, 59.2; H, 5.97; N, 17.6.

The nmr spectrum has two overlapping doublets at τ 2.23 ($J = 2.6$ cps) and τ 2.30 ($J = 2.5$ cps), each split further by 0.6 cps, a singlet at τ 3.12, a triplet at τ 3.56 ($J = 2.55$ cps), and a "triplet" at τ 9.29 in 1:1:2:1:5 ratio.

The ultraviolet spectrum has λ_{max} 287 $m\mu$ (ϵ 4300), 280 $m\mu$ (ϵ 5320), 275 $m\mu$ (ϵ 4480), and 215 (sh) $m\mu$ (ϵ 20,000).

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A Phosphorus-31 Nuclear Magnetic Resonance Study of Tertiary Phosphine Derivatives of Group VI Metal Carbonyls. III. Disubstituted Compounds¹⁻³

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The preparation, infrared spectra, and phosphorus-31 nuclear magnetic resonance spectra are reported for 15 compounds of the type *cis*- and *trans*- $L_2M(CO)_4$, where M is Cr (*trans* only), Mo, or W, and L is tributylphosphine, dibutylphenylphosphine, or diphenylbutylphosphine. Phosphorus-31-tungsten-183 spin-spin couplings, which are observed in all of the tungsten compounds, are larger for the *trans* compounds than for the corresponding *cis* compounds. This is interpreted as being consistent with the π -bonding abilities of tertiary phosphines. The phosphorus chemical shift in the *trans* compound of a particular ligand is farther downfield than that for the corresponding *cis* compound.

Introduction

In the very recent past, the concept of π bonding between phosphorus (and similar ligands) and transition metals had been accepted and was utilized to explain or partially explain various phenomena. In platinum-(II) chemistry, π bonding has been used to explain the *trans* effect,⁵ the relative thermodynamic stabilities of

cis and *trans* isomers,⁶ the greater magnitude of platinum-195-phosphorus-31 coupling constants in *cis* relative to *trans* isomers,^{7,8} and fluorine chemical shifts in fluorophenylplatinum compounds.⁹ Also, the shorter phosphorus-platinum distance in *cis*- $((CH_3)_3P)_2PtCl_2$ compared to that of the *trans* isomer could be explained by π bonding, although the original investigators¹⁰ were reluctant to do this.

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(3) Part II: S. O. Grim, D. A. Wheatland, and P. R. McAllister, *Inorg. Chem.*, **7**, 161 (1968).

(4) National Institutes of Health Predoctoral Fellow, 1965–1967.

(5) F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.*, **4**, 381 (1962).

(6) J. Chatt and R. G. Wilkins, *J. Chem. Soc.*, 273 (1952).

(7) A. Pidcock, R. E. Richards, and L. M. Venanzi, *Proc. Chem. Soc.*, 184 (1962).

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

(9) G. W. Parshall, *J. Amer. Chem. Soc.*, **88**, 704 (1966).

(10) G. G. Messmer, E. L. Amma, and J. A. Ibers, *Inorg. Chem.*, **6**, 725 (1967).

The σ -only theory, based on the polarization theory of Grinberg,^{5,11} which must be utilized to explain the strong *trans* influence of hydride, has been receiving increased attention and support for all cases, including those in which π bonding has usually been invoked. Pidcock^{12,13} and Venanzi^{12,14} have used nmr coupling constants to make a strong case for σ effects in phosphorus-platinum compounds. Zumdahl and Drago¹⁵ have recently done calculations which show little or no π bonding in phosphorus-platinum bonds. However, other recent articles still allow the possibility of π bonding in platinum compounds.^{16,17}

In the case of phosphine derivatives of metal carbonyls, there are two problems: first, similarly to the platinum question, does phosphorus π -bond with the metal, and, second, if it does, can this phenomenon be detected by infrared carbonyl stretching frequencies? It appears that the general answer is "yes" to the first question, although the tone of some articles^{18,19} is clearly anti- π . The answer used to be convincingly "yes" to the second question, with various studies in which infrared frequencies and CO force constants were used to determine the π -bonding ability of ligands in substituted metal carbonyls.²⁰⁻²² Present opinion is varied. Bigorgne^{23,24} has shown that the carbonyl stretching frequencies in phosphorus ligand nickel carbonyl derivatives are linearly related to the inductive effect (σ^*) of the groups attached to phosphorus. Since inductive effects are transmitted *via* σ bonds, it was strongly suggested that changes in $\nu(\text{CO})$'s reflect only σ -inductive character of the phosphorus ligand. Others have supported this view in varying degrees with interpretations from infrared studies.^{18,25,26} On the other hand, Graham²⁷ has extended the Cotton-Kraihanzel arguments to a tenuous extreme to obtain σ and π parameters for each ligand from infrared frequencies. Treichel²⁸ has also supported the π -bonding view by applying Graham's method to data which had been previously used¹⁸ to show that π bonding is minimal. Darensbourg and Brown²⁹ have taken an intermediate stand, *viz.*, that phosphorus π bonding is probably significant, but that it is evident not from infrared frequencies but from infrared band intensities.

(11) A. A. Grinberg, *Ann. Inst. Platine* (U.S.S.R.), **5**, 109 (1927); see C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, Inc., New York, N. Y., 1966, pp 24-30.

(12) A. Pidcock, R. T. Richards, and L. M. Venanzi, *J. Chem. Soc., A*, 1707 (1966).

(13) F. H. Allen and A. Pidcock, *ibid.*, **A**, 2700 (1968).

(14) L. M. Venanzi, *Chem. Brit.*, 162 (1968).

(15) S. S. Zumdahl and R. S. Drago, *J. Am. Chem. Soc.*, **90**, 6669 (1968).

(16) R. R. Dean and J. C. Green, *J. Chem. Soc., A*, 3047 (1968).

(17) R. J. P. Williams, *Chem. Brit.*, 277 (1968).

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

(19) R. J. Angelici and C. M. Ingemanson, *ibid.*, **8**, 83 (1969).

(20) E. W. Abel, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 2325 (1959).

(21) F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962).

(22) W. D. Horrocks, Jr. and R. C. Taylor, *Inorg. Chem.*, **2**, 723 (1963).

(23) M. Bigorgne, *J. Organometal. Chem.* (Amsterdam), **2**, 68 (1964).

(24) M. Bigorgne, *J. Inorg. Nucl. Chem.*, **26**, 107 (1964).

(25) G. R. Dobson and L. W. Houk, *Inorg. Chim. Acta*, **1**, 287 (1967).

(26) R. E. Dessy and L. Wiecek, to be submitted for publication.

(27) W. A. G. Graham, *Inorg. Chem.*, **7**, 315 (1968).

(28) R. P. Stewart and P. M. Treichel, *ibid.*, **7**, 1942 (1968).

(29) D. J. Darensbourg and T. L. Brown, *ibid.*, **7**, 959 (1968).

In view of this present relative uncertainty over interpretation of infrared data, we thought that other physical data could contribute constructively to the controversy of phosphorus π bonding in metal carbonyls. The phosphorus-tungsten coupling constant is a value which arises directly from the bond in question, *i.e.*, between phosphorus and tungsten, and therefore relates directly to the properties of the bond, in contrast to carbonyl stretching frequencies which are properties of bonds which are two bonds removed from the bond in question.

We report here the results of a study of the group VI metal hexacarbonyls which are disubstituted by tertiary phosphines to give *cis* and *trans* isomers. This is a continuation of earlier work on the phosphorus-31 magnetic resonance of coordination compounds,^{3,8,30-32} which has shown phosphorus-31 nmr to be useful for stereochemical and bonding studies of these compounds. The phosphorus-31 nmr signals of the tungsten compounds are split by tungsten-183 (natural abundance, 14.3%; nuclear spin, $1/2$) into a 7:86:7 triplet from which J_{W-P} is obtained.³³ The principal purpose of the investigation was to determine if the relative magnitudes of J_{W-P} for the *cis*- and *trans*-disubstituted compounds are consistent with the π -bonding theory.

Experimental Section

Phosphorus-31 nmr measurements were carried out on a Varian DP-60 instrument at 24.3 MHz. Chemical shifts (ppm vs. H_3PO_4) are accurate to ± 0.3 ppm and coupling constants are accurate to ± 8 cps. The infrared spectra in the carbonyl stretching region were measured in cyclohexane solution (contained in a sodium chloride cell with a thickness of 0.012 mm) with a Perkin-Elmer Model 621 ir spectrometer. The spectra were calibrated by saturated water vapor lines at 1942.6, 1919.0, and 1889.6 cm^{-1} . Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn. Tributylphosphine was donated by M & T Chemicals. The other phosphines were prepared by standard Grignard techniques.³⁴ Chromium and molybdenum hexacarbonyls were purchased from A. D. MacKay, Inc. Tungsten hexacarbonyl was purchased from Pressure Chemical Co.

Preparations of the coordination compounds were similar to the method of Magee and coworkers.³⁵ In general, the metal carbonyl (about 10 g) was heated in 50 ml of diethylene glycol dimethyl ether (diglyme) under N_2 to about 160°, and the tertiary phosphine was injected through a serum cap on a side arm of the reaction flask. The molar ratio of phosphine to metal carbonyl was 2:1. The progress of the reaction was followed crudely by the collection of evolved CO in a buret inverted in a beaker of oil.

When the evolution of CO ceased, the solvent was removed by vacuum distillation and the residue was dissolved in a minimum amount of CH_2Cl_2 . Subsequent addition of methanol and chilling at 0° caused crystallization of the crude product.

It was necessary to analyze all crude products to estimate the amounts of *cis* and/or *trans* isomers present. This could be done quickly by examination of the infrared spectrum of a cyclohexane

(30) S. O. Grim and R. A. Ference, *Inorg. Nucl. Chem. Letters*, **2**, 205 (1966).

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

(32) S. O. Grim, P. R. McAllister, and R. M. Singer, *Chem. Commun.*, 38 (1969).

(33) S. O. Grim, W. McFarlane, and D. A. Wheatland, *Inorg. Nucl. Chem. Letters*, **2**, 49 (1966).

(34) K. D. Berlin, T. H. Austin, M. Peterson, and M. Nagabhushanam, "Topics in Phosphorus Chemistry," Vol. 1, M. Grayson and E. J. Griffith, Ed., Interscience Publishers, New York, N. Y., 1964, p 17.

(35) T. A. Magee, C. N. Matthews, T. S. Wang, and J. H. Wotiz, *J. Am. Chem. Soc.*, **83**, 3200 (1961).

TABLE I
 PREPARATIVE AND ANALYTICAL DATA FOR $L_2M(CO)_4$

Compound	Yield, %	Color	Mp, °C	% carbon		% hydrogen	
				Calcd	Found	Calcd	Found
<i>trans</i> -((C ₄ H ₉) ₃ P) ₂ Cr(CO) ₄	85	Yellow	40-41	59.1	59.2	9.6	9.7
<i>trans</i> -(C ₆ H ₅ C ₄ H ₉ P) ₂ Cr(CO) ₄	20	Yellow	108-109	63.1	63.3	7.6	7.7
<i>trans</i> -((C ₆ H ₅) ₂ C ₄ H ₉ P) ₂ Cr(CO) ₄	30	Yellow	155-157 dec	66.7	66.5	5.9	5.9
<i>cis</i> -((C ₄ H ₉) ₃ P) ₂ Mo(CO) ₄	9	Colorless	32	54.9	54.7	8.9	8.8
<i>trans</i> -((C ₄ H ₉) ₃ P) ₂ Mo(CO) ₄	20	Yellow	44-45	54.9	54.8	8.9	8.7
<i>cis</i> -(C ₆ H ₅ (C ₄ H ₉) ₂ P) ₂ Mo(CO) ₄	15	Colorless	99-100	58.9	59.1	7.1	7.3
<i>trans</i> -((C ₆ H ₅ (C ₄ H ₉) ₂ P) ₂ Mo(CO) ₄	5	Yellow	103-104	58.9	59.0	7.1	7.3
<i>cis</i> -((C ₆ H ₅) ₂ C ₄ H ₉ P) ₂ Mo(CO) ₄	19	Colorless	154-156 dec	62.4	62.5	5.5	5.6
<i>trans</i> -((C ₆ H ₅) ₂ C ₄ H ₉ P) ₂ Mo(CO) ₄	12	Yellow	160-163 dec	62.4	62.4	5.5	5.6
<i>cis</i> -((C ₄ H ₉) ₃ P) ₂ W(CO) ₄	5	Colorless	37-38	48.0	47.8	7.8	7.8
<i>trans</i> -((C ₄ H ₉) ₃ P) ₂ W(CO) ₄	35	Yellow	46-47	48.0	48.2	7.8	7.8
<i>cis</i> -(C ₆ H ₅ (C ₄ H ₉) ₂ P) ₂ W(CO) ₄	24	Colorless	107-108	51.9	52.0	6.3	6.4
<i>trans</i> -(C ₆ H ₅ (C ₄ H ₉) ₂ P) ₂ W(CO) ₄	13	Yellow	103-104	51.9	51.7	6.3	6.2
<i>cis</i> -((C ₆ H ₅) ₂ C ₄ H ₉ P) ₂ W(CO) ₄	27	Colorless	157-159 dec	55.4	55.2	4.9	5.1
<i>trans</i> -((C ₆ H ₅) ₂ C ₄ H ₉ P) ₂ W(CO) ₄	21	Yellow	175-176	55.4	55.6	4.9	5.1

 TABLE II
 INFRARED AND ³¹P NMR DATA FOR $L_2M(CO)_4$ ^a

Compound	Carbonyl str freq, cm ⁻¹	Chem shift, ppm			<i>J</i> _{W-P} , cps
		Free ligand	Compound	Coordn	
<i>trans</i> -((C ₄ H ₉) ₃ P) ₂ Cr(CO) ₄	1875 vs	32.3	-44.2	-76.5	
<i>cis</i> -(C ₆ H ₅ (C ₄ H ₉) ₂ P) ₂ Cr(CO) ₄ ^b	2002 m, 1906 s, 1893 s, 1874 s	26.2	-32.4	-58.6	
<i>trans</i> -(C ₆ H ₅ (C ₄ H ₉) ₂ P) ₂ Cr(CO) ₄	1882 vs	26.2	-50.4	-76.6	
<i>trans</i> -((C ₆ H ₅) ₂ C ₄ H ₉ P) ₂ Cr(CO) ₄	1890 vs	17.1	-61.5	-78.6	
<i>cis</i> -((C ₄ H ₉) ₃ P) ₂ Mo(CO) ₄	2015 m, 1913 s, 1899 s, 1886 s	32.3	-8.9	-41.2	
<i>trans</i> -((C ₄ H ₉) ₃ P) ₂ Mo(CO) ₄	1884 vs	32.3	-22.4	-54.7	
<i>cis</i> -(C ₆ H ₅ (C ₄ H ₉) ₂ P) ₂ Mo(CO) ₄	2016 m, 1917 s, 1902 s, 1888 s	26.2	-14.5	-40.7	
<i>trans</i> -(C ₆ H ₅ (C ₄ H ₉) ₂ P) ₂ Mo(CO) ₄	1893 vs	26.2	-28.8	-55.0	
<i>cis</i> -((C ₆ H ₅) ₂ C ₄ H ₉ P) ₂ Mo(CO) ₄	2021 m, 1924 s, 1904 s, 1892 s	17.1	-25.8	-42.9	
<i>trans</i> -((C ₆ H ₅) ₂ C ₄ H ₉ P) ₂ Mo(CO) ₄	1900 vs	17.1	-38.9	-56.0	
<i>cis</i> -((C ₄ H ₉) ₃ P) ₂ W(CO) ₄	2012 m, 1908 s, 1889 s, 1882 s	32.3	10.0	-22.3	225
<i>trans</i> -((C ₄ H ₉) ₃ P) ₂ W(CO) ₄	1879 vs	32.3	2.5	-29.8	265
<i>cis</i> -(C ₆ H ₅ (C ₄ H ₉) ₂ P) ₂ W(CO) ₄	2016 m, 1911 s, 1894 s, 1886 s	26.2	4.0	-22.2	220
<i>trans</i> -(C ₆ H ₅ (C ₄ H ₉) ₂ P) ₂ W(CO) ₄	1885 vs	26.2	-4.0	-30.2	270
<i>cis</i> -((C ₆ H ₅) ₂ C ₄ H ₉ P) ₂ W(CO) ₄	2018 m, 1918 s, 1898 s, 1890 s	17.1	-8.2	-25.3	230
<i>trans</i> -((C ₆ H ₅) ₂ C ₄ H ₉ P) ₂ W(CO) ₄	1892 vs	17.1	-14.4	-31.5	275

^a Abbreviations: m, medium; s, strong; vs, very strong. ^b Observed but not isolated.

spectra of each crude product. In general, the *trans*-isomer spectra consist of only a strong band somewhat below 1900 cm⁻¹ while the *cis*-isomer spectra consist of one medium band slightly above 2000 cm⁻¹ and three stronger bands around 1900 cm⁻¹. The qualitative analysis of these *cis* and *trans* isomers was based upon the work of Poilblanc and Bigorgne.³⁰

The infrared spectra of the crude products indicated either a mixture of *cis* and *trans* isomers or only the *trans* isomers in some cases (Cr). If only the *trans* isomer was present, the crude product was recrystallized from a CH₂Cl₂-CH₃OH mixture, collected by vacuum filtration, and dried in a vacuum oven at 40° (6 Torr).

In those cases where both *cis* and *trans* isomers were present in the crude product, separation was achieved by column chromatography. The column (70 × 3 cm) was packed almost half-full with Alcoa Chromatographic alumina (F-20). The crude product was dissolved in light petroleum ether (bp 30-60°) and placed on the column. The column was eluted with light petroleum ether and 50-ml portions were collected in 100-ml round-bottomed flasks equipped with 24/40 joints. The petroleum ether was removed with a rotary evaporator and the residues were dissolved in CH₂Cl₂. Addition of CH₃OH to the solutions caused crystallization of the eluted products. These were collected by vacuum filtration and dried in a vacuum oven. An infrared spectrum in the carbonyl region was taken of each of the successive eluted fractions. These spectra were used to monitor the separation of the isomers.

In all of the cases of mixtures of *cis* and *trans* isomers which

were reported, a yellow band was eluted first and this band was found to contain the *trans* isomer. Continued elution yielded a faintly gray band which was found to contain the *cis* isomer.

Eluted sample fractions whose infrared spectra exhibited no impurities were then collected together to determine the yields. Most mixtures separated quite cleanly and were analytically pure without further recrystallization.

The yields and analytical data for the compounds prepared in this study are given in Tables I and II. The compounds are quite air stable as crystalline solids but their solutions decompose after several hours at room temperature in the air. Samples of these compounds can be stored in dark glass bottles and kept in a cool dark place with no noticeable decomposition after several months.

Results and Discussion

The phosphorus-31 nmr data are reported in Table II. Several observations can be made. First, the coordination chemical shifts (absolute values) are in the order Cr > Mo > W, which is the same as observed for the monosubstituted compounds.³¹ Second, the ³¹P chemical shift of the *trans* compound is considerably downfield from the *cis* compound of the same metal and same ligand. This is an observation which has been useful for qualitative identification of compounds and estimation of product ratios in crude reaction mixtures of metal carbonyls with phosphines. Third, *J*_{W-P}

for *trans* compounds is larger than J_{W-P} for *cis* compounds. Fourth, unlike the results for the mono-substituted compounds, J_{W-P} does not change appreciably from ligand to ligand for compounds of the same stereochemistry. The experimental errors are about the same magnitude as the differences in measurements for the compounds, so no conclusion can be made on the fourth point.

However, the difference noted between the coupling constants for the compounds of different stereochemistry is real, and *trans* J_{W-P} is greater than *cis* J_{W-P} for $(R_3P)_2W(CO)_4$. This is to be compared to $(R_3P)_2PtCl_2$ for which *cis* J_{Pt-P} is greater than *trans* J_{Pt-P} .^{7,8,12}

We feel both of these facts are consistent with the π -bonding explanation. Phosphorus competes more effectively with chlorine *trans* to it for platinum d_{π} electrons in the *cis* isomer than it competes with itself in the *trans* isomer, and phosphorus competes more effectively for tungsten d_{π} electrons *trans* to itself in the *trans* isomer compared to carbon monoxide *trans* to it in the *cis* isomer.³⁷

The assumption here is that the π -acceptor abilities are in the order $CO > P > Cl$, for which there is ample evidence.³⁸ Moreover, the greater the π bonding becomes, the greater is the phosphorus-metal interaction and the greater is the metal-phosphorus coupling as a result.

We are not prepared at this time to propose an explanation for the greater downfield chemical shift of the phosphorus in the *trans* isomer, except to point out that it probably does not arise mainly from diamagnetic shielding effects as was suggested in the platinum cases.⁸ Results with palladium and rhodium complexes³⁹ indicate also that simple diamagnetic effects are not sufficient to explain the ³¹P shifts, as has been emphasized for other types of phosphorus compounds.⁴⁰

(37) S. O. Grim and D. A. Wheatland, *Inorg. Nucl. Chem. Letters*, **4**, 187 (1968).

(38) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience Publishers, New York, N. Y., 1966, pp 719-759.

(39) S. O. Grim, R. L. Keiter, and R. A. Ference, to be submitted for publication.

(40) J. H. Letcher and J. R. Van Wazer, "Topics in Phosphorus Chemistry," Vol. 5, M. Grayson and E. J. Griffith, Ed., Interscience Publishers, New York, N. Y., 1967, Chapter 2.

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Aryl-Substituted Phosphonitrilic Fluorides. IV. The Crystal and Molecular Structure of 1,1-Diphenylphosphonitrilic Fluoride Trimer¹

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The crystal structure of the 1,1-diphenylphosphonitrilic fluoride trimer, $1,1-N_3P_3F_4(C_6H_5)_2$, has been determined by symbolic addition and Fourier techniques. The results have been refined to a conventional R factor of 0.059 by a full-matrix least-squares treatment employing anisotropic temperature factors on 2442 reflections measured by counter methods. The crystals belong to the orthorhombic system, with $a = 14.803$ (4), $b = 12.571$ (5), $c = 16.732$ (8) Å; the space group is $Pnma$, and there are eight molecules in the unit cell ($\rho_{measd} = 1.54$ g cm⁻³, $\rho_{calcd} = 1.56$ g cm⁻³). The asymmetric unit contains two independent molecules each of which has C_s crystallographic symmetry. The phosphorus-nitrogen ring has five atoms approximately coplanar, with the phenyl-substituted phosphorus atom 0.20 Å out of this plane. There are three different sets of phosphorus-nitrogen bonds with mean lengths 1.618 (5), 1.558 (4), and 1.539 (5) Å. The exocyclic bond angles are: C-P-C, 107.9 (3)°; F-P-F, 96.9 (2)°. The endocyclic angles are: N-P-N, 115.5 (3)°; 120.6 (3)°; P-N-P, 120.5 (2)°.

Introduction

The investigation of crystal structures of phosphonitrilic halides and their derivatives is of interest for both theoretical considerations and elucidation of stereochemical substitution patterns. The diphenylphosphonitrilic fluoride trimer obtained from the Friedel-Crafts reaction of benzene with the monophenylphosphonitrilic fluoride trimer has been assigned a geminal configuration on the basis of chemical¹ and nuclear magnetic resonance^{1,4} evidence. We have investigated the crystal structure of this compound in order

to verify the geminal assignment and to investigate further the influence of fluorine as an exocyclic group on the conformation of the phosphorus-nitrogen ring system. The difference between fluorine- and chlorine-substituted phosphonitrilic halides is often dramatic; *e.g.*, tetrameric phosphonitrilic chloride exists in two forms, one with a boat⁵ and the other with a chair⁶ configuration, whereas tetrameric phosphonitrilic fluoride⁷ is planar. Inasmuch as the crystal structure of the 1,1-diphenylphosphonitrilic chloride trimer has been determined,⁸ a comparison with the corresponding fluoride is of some

(1) Part III: C. W. Allen, F. Y. Tsang, and T. Moeller, *Inorg. Chem.*, **7**, 2183 (1968).

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(4) C. W. Allen and T. Moeller, *Inorg. Chem.*, **7**, 2177 (1968).

(5) R. Hazekamp, T. Migchelsen, and A. Vos, *Acta Cryst.*, **15**, 539 (1962).

(6) A. J. Wagner and A. Vos, *ibid.*, **B24**, 707 (1968).

(7) H. McD. McGeachin and F. R. Tromans, *J. Chem. Soc.*, 4777 (1961).

(8) N. V. Mani, F. R. Ahmed, and W. H. Barnes, *Acta Cryst.*, **19**, 693 (1965).