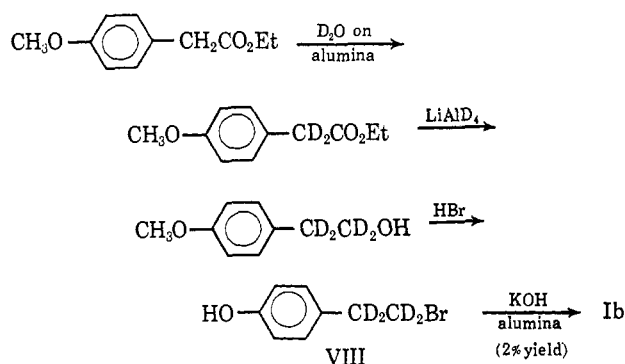


Table I. Mass Spectroscopic Results^a

Compound	Peaks analyzed ^a	Isotopic distribution, mole %					Total excess D content, % ^b
		D ₀	D ₁	D ₂	D ₃	D ₄	
VIII	200-206	1.31	0.51	10.6	37.2	50.5	84.6 ± 0.4
	121-125	1.54	1.4	12.2	37.4	47.3	81.8
	107-109	6.1	19.9	73.8	84.0
IIb	122-126	1.4	1.2	10.3	36.0	51.2	83.7 ± 1.7
	107-109	5.14	18.9	75.9	85.5
IVb	194-198	3.4	1.9	11.7	35.4	47.7	80.8 ± 0.8
	107-109	12.1	25.2	62.7	75.5
Vb	194-198	3.31	0.70	12.3	39.8	44.0	80.5 ± 0.5
	122-126	4.55	6.77	12.0	36.8	39.9	75.0

^a Calculated after comparison with the protium compound spectrum as per procedure described in K. Biemann, "Mass Spectrometry: Organic Chemical Applications," McGraw-Hill Book Co., Inc., New York, N. Y., 1962. ^b On the basis of replacement of four protons.

Ib was prepared by the following route, adapted from the synthesis of Ia.^{8,8}



The photolysis of Ib in ethyl ether was carried out as reported previously,³ and the products were collected by preparative gas-liquid partition chromatography. The very small quantities of separated products IIb, IVb, and Vb were identified by comparison with IIa, IVa, and Va³ and were analyzed for deuterium distribution by mass spectrometry⁹ and nuclear magnetic resonance. The nmr spectra obtained using a time averaging computer¹⁰ were compatible with the mass spectrometric results, but were not definitive in themselves. The pertinent mass spectroscopic data are given in Table I. The total per cent of excess deuterium in the dienone precursor 2-(*p*-hydroxyphenyl)ethyl bromide (VIII) as found by mass spectrometry agreed well with an independent analytical determination of 85.0%.

It is clear from the data in Table I that products IIb, IVb, and Vb are formed by routes that lead to retention of at least 95% of the original isotopic content. Moreover, the distribution of deuterium is almost exactly as predicted by the diradical mechanism and provides direct evidence for the formation of V by a 1,2-H(D) migration mechanism and not by a series of hydrogen (deuterium) abstraction steps. Also, II is seen to arise solely *via* VI, and not VII.

(8) R. Baird and S. Winstein, *J. Am. Chem. Soc.*, **85**, 567 (1963).

(9) Analyses at Columbia University on a Hitachi-Perkin-Elmer Model RMU-6D mass spectrometer operating at 13 and 75 v. with a heated inlet system at 100°. The protium compounds were analyzed as controls at the same time as the deuterium compounds. A discussion of the interesting fragmentation patterns will be reported in a later paper.

(10) These spectra were obtained at the Union Carbide Research Laboratories, Tarrytown, N. Y., through the generosity of Dr. Donald Arnold, Dr. Earl Whipple, and Mr. Mike Ruta. We are deeply grateful to these gentlemen for these measurements.

Further evidence for the lack of involvement of intermolecular hydrogen abstraction in the formation of V was the observation that the ratio V/IV was not increased on photolysis of Ia in the presence of excess *p*-ethylphenol (IIa). If anything, the ratio V/IV decreased in this experiment.

The intramolecular 1,2-hydrogen-atom shift demonstrated in this case is in contrast with the well-known lack of such processes in ground-state radical chemistry in solution.⁵⁻⁷ This suggests that an important driving force which provides much-needed stabilization for the transition state for such a rearrangement¹¹ is the formation of a structure in which all electrons are paired (in this case VII) from a diradical (in this case VI).¹² This is an added argument in favor of diradical VI as a reactive intermediate in the photochemistry of I. This type of rearrangement is probably general⁴ and should be observed in other favorable systems.

(11) H. E. Zimmerman and A. Zweig, *J. Am. Chem. Soc.*, **83**, 1196 (1961).

(12) It could be argued that the hydrogen migration is facilitated by dipolar contributions to the diradical VI (however, see ref 3), although this argument would clearly not be applicable to the rearrangements reported by Griffin, *et al.*⁴ It has been suggested by a referee that such dipolar contributions would be significantly more important for VI generated from singlet- rather than triplet-excited states, although this is a subject of much debate at this time. This matter will be discussed fully in a later paper in this series, along with results of excited-state studies in this system now in progress.

(13) National Institutes of Health Predoctoral Fellow, 1965 to present

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 Received May 7, 1966

Fluorine-19 Nuclear Magnetic Resonance Studies of π Interactions in Pentafluorophenylphosphines and Their Complexes. A Correlation of Coupling Constants with Chemical Shifts

Sir:

The nature of the metal-ligand interaction is a principal concern of coordination chemistry. Recently, in an important extension of the approach developed by Taft¹ for organic compounds, Parshall² has shown that the F¹⁹ chemical shifts of monofluorophenylplatinum(II) complexes can provide a valuable insight into the electronic character of the bond between platinum and its anionic ligands.

(1) R. W. Taft and J. W. Rakshys, Jr., *J. Am. Chem. Soc.*, **87**, 4387 (1965), and references cited therein.

(2) G. W. Parshall, *ibid.*, **86**, 5367 (1964); **88**, 704 (1966).

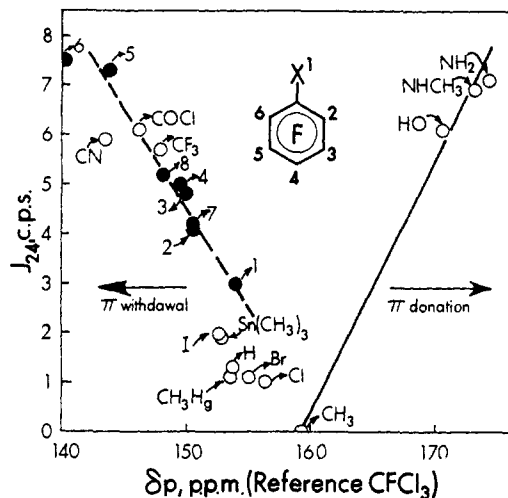


Figure 1. Relation between *o*-fluorine-*p*-fluorine coupling constant (J_{24}) and chemical shift of *p*-fluorine (δ_p). Closed circles refer to compounds of Table I; other points are from this work and the literature: N. Boden, *et al.*, *Mol. Phys.*, 8, 133 (1964); I. J. Lawrenson, *J. Chem. Soc.*, 1117 (1965).

The nmr spectra of pentafluorophenyl derivatives should give added information owing to changes in coupling constants, as well as in chemical shifts. This is illustrated in Table I, where we report F^{19} nmr data for various new pentafluorophenylphosphines and their complexes.³ Combining this with data from the literature, we have established a linear relationship between the chemical shift of the *p*-fluorine (δ_p) and the coupling constant between the *o*- and *p*-fluorines (J_{24}), as shown in Figure 1. While this relationship should be of particular interest in development of the theory of spin-spin interaction in the phenyl system, we have used it empirically to elucidate π interactions in organometallic compounds.

Table I. Chemical Shifts and Coupling Constants for Pentafluorophenylphosphine Derivatives^a

Compound	δ_p^b	J_{24}^c	J_{14}^c	J_{12}^c
1 $C_6F_5P(CH_3)_2$	153.9	3.0	0.4	29.4
2 $C_6F_5P(C_6H_5)_2$	150.6	4.1	0.6	38.9
3 $C_6F_5P(C_6H_5)_2-Mo(CO)_5$	150.0	4.8	1.6	<2
4 $C_6F_5P(C_6H_5)_2-Fe(CO)_4$	149.5	5.0	1.8	<3
5 $C_6F_5P(C_6H_5)_2-BCl_3$	143.8	7.3	3.1	14
6 $[C_6F_5P(C_6H_5)_2H]^+Cl^-$	140.4	7.5	2.7	13
7 $(C_6F_5)_2PC_6H_5$	150.5	4.2	<1	31.1
8 $(C_6F_5)_2PC_6H_5-Mo(CO)_5$	148.1	5.2	1.4	5

^a Measured in 20–30% (w/v) solutions in benzene with C_6F_5 internal standard; converted to CCl_3 scale by adding 163.0 ppm.

^b Chemical shift of *p*-fluorine. ^c Coupling constants in cps. See Figure 1 for numbering system.

In both monofluorophenyl¹ and pentafluorophenyl⁴ systems, δ_p depends on the Hammett-Taft functions σ_{R^0} and σ_1 , the resonance and inductive effect parameters, respectively. We conclude from the available data that δ_p is determined largely by σ_{R^0} alone, so that,

(3) Details of the preparation, infrared spectra, and nmr spectral analysis will be published shortly.

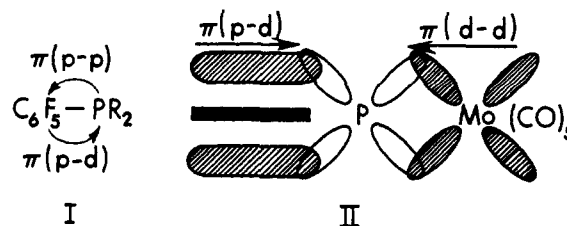
(4) I. J. Lawrenson, *J. Chem. Soc.*, 1117 (1965),

to a first approximation, δ_p is a measure of π interaction between the pentafluorophenyl ring and its substituent.⁵ Since we have found that J_{24} is related linearly to δ_p , this coupling constant is also a measure of π interaction. Furthermore, we suggest that the relation of J_{24} to δ_p (Figure 1) distinguishes between π -electron donation to the ring and π -electron withdrawal from the ring by the substituent group.

For example, substituents giving low δ_p and high J_{24} values (C_6F_5-CN) must be considered strong π -electron acceptors. Substituents giving high δ_p and high J_{24} values are those ($C_6F_5-NH_2$) which could only function as π donors. Intermediate δ_p and low J_{24} values imply a weak π interaction ($C_6F_5-CH_3$).

In the case of the phosphines, coupling between the phosphorus and *p*-fluorine (J_{14}) parallels J_{24} . Not only are there now three parameters sensitive to π interactions, but the coupling constants J_{24} and J_{14} may have the advantage of being less sensitive to inductive effects than δ_p .

Relating this argument to the compounds of Table I, we find that the phosphines lie on the π withdrawal side of Figure 1, in contrast to amines; one presumes that lone-pair donation to the ring (a $\pi(p-p)$ effect) is outweighed by back-donation to phosphorus (a $\pi(p-d)$ effect), in which the vacant phosphorus 3d orbitals accept electrons from the ring. These opposing effects are shown schematically in I.



Comparing next the phosphine $C_6F_5P(C_6H_5)_2$ (point 2 of Figure 1) with its boron trichloride complex (point 5 of Figure 1), we infer a greater net π withdrawal in the complex because of its lower δ_p and higher J_{24} and J_{14} values. In the complex, no lone pair is available for donation to the ring, and $\pi(p-d)$ withdrawal is the principal effect.

The complex $C_6F_5P(C_6H_5)_2Mo(CO)_5$ (point 3, Figure 1) occupies an intermediate position in Figure 1, indicating a net π withdrawal intermediate between that of the free phosphine and its boron trichloride complex. In terms of the generally accepted picture of the bonding in metal carbonyls,⁶ as represented schematically in II, the d electrons of molybdenum and the π electrons of the C_6F_5 ring compete for access to the vacant d orbitals of phosphorus. There is, of

(5) In pentafluorophenylboron compounds, a sensitivity of δ_p to the interaction of phenyl π electrons with the boron p orbital has been noted: R. D. Chambers and T. Chivers, *ibid.*, 3933 (1965).

(6) For example, cf. F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Division of John Wiley and Sons, Inc., New York, N. Y., 1962, Chapter 27. We draw attention in particular to the statement, "Although it has not so far been possible to detect the $\sigma-\pi$ synergic bonding in complexes with P, As, or S donors by infrared spectra, as can be done for CO or CNR using C-O or C-N stretching frequencies, it is generally assumed that some π bonding occurs; however, it is quite small except where the attached groups are highly electronegative" (p 625, italics theirs). The C_6F_5 group is quite electronegative and would thus enhance the π bonding. The results reported here provide what is perhaps the most convincing direct evidence thus far advanced for the π -acceptor aspect of the synergic bond.

course, no such competition in the boron trichloride complex, which accounts for the greater π withdrawal.

Also of interest is the decrease in the phosphorus-*o*-fluorine coupling constant (J_{12}) when the phosphines form complexes, an effect that is especially marked in metal carbonyl complexes.⁷

Acknowledgment. We thank the National Research Council of Canada and the Defense Research Board of Canada (Grant No. 9530-49) for financial support.

(7) NOTE ADDED IN PROOF. We have now shown by double-irradiation techniques that J_{24} for $C_6F_5NH_2$ and C_6F_5COCl are of opposite sign. It appears most probable that, in general, the sign of J_{24} is opposite for π -withdrawing substituents and π -donating substituents. Figure 1 thus reduces to a single straight line, for which the least-squares equation is $J_{24} = -0.4706\delta_p + 74.64$. We have learned that Professor F. G. A. Stone (private communication; *J. Chem. Soc.*, in press) has attempted to relate $\delta_p - \delta_m$ in pentafluorophenylplatinum complexes to π -bonding effects.

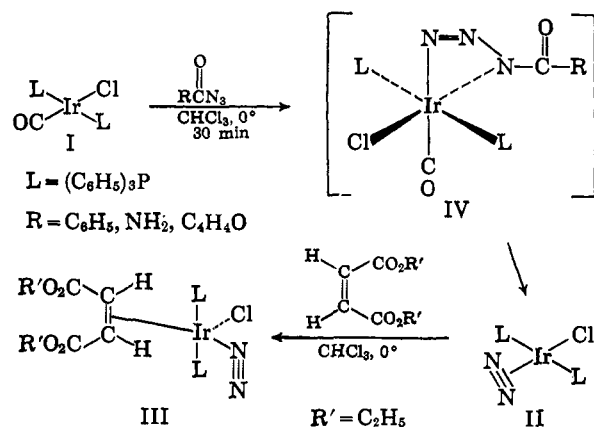
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Received May 21, 1966

Iridium Complexes of Molecular Nitrogen

Sir:

In the course of our current exploration¹ of oxidative addition reactions of complexes having a d^8 configuration we have discovered two remarkable compounds in which molecular nitrogen is apparently bound to iridium. These compounds (II and III) represent the second reported instance of complexed nitrogen inasmuch as Allen and Senoff have recently described² the preparation of a cationic ruthenium(II) complex which is also thought to contain coordinated nitrogen.



Aside from the novel nature of these nitrogen compounds, their significance stems from the possibility that such complexes may lead to the development of homogeneous catalysts for the hydrogenation of nitrogen. Attempts to "fix" nitrogen are being made in laboratories throughout the world.

The discovery of the iridium-nitrogen complexes II and III ensued from our unsophisticated hypothesis that "unsaturated" d^8 complexes such as Vaska's³ iridium(I) compound (I) are analogous to olefins in their chemical reactions. In an effort to prepare 1,3-dipolar adducts, the pseudo-olefinic complex I was treated with a series

of acid azides. Whenever these reactions were carried out at 0°, the same golden yellow compound (II) was obtained (by precipitation with hexane) regardless of the azide employed. Structure II provisionally assigned to this complex is based on the following data. *Anal.* Calcd for $C_{36}H_{30}ClN_2P_2Ir$: C, 55.38; H, 3.84; N, 3.58; Cl, 4.61; P, 7.94. Found: C, 54.95; H, 3.98; N, 3.47; Cl, 5.06; P, 7.60. The infrared spectrum of II exhibits an intense absorption at 2095 cm^{-1} which is assigned to coordinated N_2 . Other than a weak band⁴ at 1970 cm^{-1} , no absorption bands are present in the region $3000\text{--}1600\text{ cm}^{-1}$. The yellow complex II slowly decomposes in the solid state at room temperature evolving a gas and affording a green-gray, soluble solid of uncertain structure.⁵ In a similar manner, solutions of II in chloroform or benzene decompose in 1–2 hr at room temperature evolving a gas. The intense infrared peak at 2095 cm^{-1} is lost during these decompositions. The yellow solid II was decomposed at 110° in a sealed flask under argon, and the evolved gas was found to be nearly pure nitrogen by analysis on a gas chromatographic column packed with a molecular sieve. Treatment of a $CHCl_3$ solution of II with a $CHCl_3$ solution of triphenylphosphine results in the immediate, vigorous evolution of nitrogen (gas chromatographic analysis) and the formation of a red solution. Presumably, chlorotris(triphenylphosphine)iridium(I) (analogous to the rhodium complex described by Wilkinson⁶ as a homogeneous hydrogenation catalyst) is formed in this reaction. When solutions of the yellow solid are treated with carbon monoxide, a colorless intermediate is first formed⁷ and subsequently decomposes to form Vaska's compound (I). Acetylenes, alkyl halides, hydrogen chloride, mercuric chloride, and carbon tetrachloride react with II, nitrogen is evolved, and new complexes are formed.

The formation of the nitrogen complex II from acid azides may involve a 1,3-dipolar intermediate such as IV which could form II by elimination of N-acyl isocyanate.⁸ This speculation is supported by our inability to detect CO in the argon atmosphere over the mixture during the entire course of the reaction. Experiments in progress are designed to test further this hypothesis.

Treatment of the yellow complex II with diethyl maleate afforded a more stable pale yellow complex, which is thought to have the structure depicted for III. *Anal.* Calcd for $C_{44}H_{42}ClN_2O_4P_2Ir$: C, 55.46; H, 4.41; N, 2.94; Cl, 3.78; P, 6.51. Found: C, 55.32; H, 4.55; N, 3.05; Cl, 3.99; P, 6.57. The infrared spectrum (KBr) of III exhibits a single intense band at 2190 cm^{-1} , but no other absorption is found in the $2800\text{--}1800\text{-cm}^{-1}$ region. A strong doublet at 1735 and 1695 cm^{-1} is assigned to the ester groups. The shift of the coordinated nitrogen absorption from 2095 to 2190 cm^{-1} is surprising but can be rationalized in

(4) We have no explanation for this absorption except that it may be an impurity.

(5) Molecular weight measurements suggest this is a trimer containing metal-metal bonds.

(6) J. F. Young, J. A. Osborn, F. H. Jardine, and G. Wilkinson, *Chem. Commun.*, 131 (1965).

(7) This is probably a five-coordinate complex containing two CO groups such as reported by L. Vaska, *Science*, **152**, 769 (1966).

(8) A reaction whereby a metal carbonyl reacts with azide ion to form N_2 and a metal N-isocyanate⁹ may be related to our current observation.

(9) W. Beck and H. S. Smedal, *Angew. Chem.*, **78**, 267 (1966).

(1) J. P. Collman and W. R. Roper, *J. Am. Chem. Soc.*, **87**, 4008 (1965); **88**, 180 (1966); **88**, 3504 (1966); *Chem. Commun.*, 244 (1966).

(2) A. D. Allen and C. V. Senoff, *ibid.*, 621 (1965).

(3) L. Vaska and J. W. Diluzio, *J. Am. Chem. Soc.*, **83**, 2784 (1961).