cooling at −10°, greenish yellow crystals of K[(β-oxoethyl)(acac)-PtCl] were filtered off, washed with ether, and dried *in vacuo*, yield 18.17 mg (52.5%, 170–175° dec (yellow to black)). Repeated recrystallization results in a bright yellow product.

This is converted to the desired π-enol complex by dissolution in a minimum amount of water and acidification with 3 *N* HCl nearly quantitatively precipitating (π-C₂H₃OH)(acac)PtCl.

(π-C₃H₅OH)(acac)PtCl, Preparation *via* the β-Oxopropyl Complex. (a) β-Oxopropyl Complex. Aqueous potassium hydroxide, 0.5 ml of 0.680 *N* (340 μmol), was added to an acetone solution of chloro(acetylacetonato)(ethylene)platinum(II), 100.7 mg (282 μmol) in 10 ml of acetone. After 30 min at room temperature, the solution was evaporated to dryness under reduced pressure. The resulting yellow crystalline residue, thoroughly dried *in vacuo*, was then dissolved in a minimum amount of warm acetone and recrystallized by slowly adding an equal volume of 1:1 ether–hexane and cooling at 0°, yield of potassium chloro(acetyacetonato)(β-oxopropyl)platinum(II) 105 mg (87.5%), 158–172° dec (yellow to black). *Anal.* Calcd for K[C₈H₁₂O₃PtCl]: C, 22.6; H, 2.84; Pt, 45.8; Cl, 8.33. Found: C, 22.8; H, 2.68; Pt, 46.6; Cl, 9.46. Infrared spectrum (KBr pellet, Beckman IR-8): 3090 w, 3020 w, 2960 m, 2920 m, 2840 w, 1645 s, 1560 s, 1540 s, 1520 s, 1425 s, 1383 s, 1362 s, 1348 s, 1275 m, 1248 s, 1202 m, 1108 m, 1073 m, 1028 m, 1015 m, 1007 m, 960 w, 944 w, 924 w, 778 s, 697 w, 657 w, 646 w, 627 s cm⁻¹. Proton nmr spectrum (Varian T-60, in D₂O *vs.* external TMS): 2.42 (6 Hₐ, s), 2.75 (3 Hᵦ, s), 3.94 (2 Hᵨ, s), and 6.16 (1 H_d, S) ppm. Each singlet was accompanied by ¹⁹⁵Pt satellites, and the observed ¹⁹⁵Pt–H coupling constants were <5, 18, 116 and 8 Hz, respectively.

(b) π-Propen-2-ol Complex. To a suspension of 50.03 mg (117 μmol) of the β-oxopropyl complex in 17 ml of dry ether was added 0.35 ml of dry THF (0.40 *M*) in HCl (140 μmol of HCl). The mixture was stirred for 30 min at room temperature. Then the yellow ether solution was decanted from the residue of unprotonated starting material and evaporated under reduced pressure to a volume of 1 ml. To this, 2 ml of hexane was slowly added and the solution was then cooled at −18°, producing a light yellow crystalline precipitate. This was washed twice under argon with dry 1:3 ether–hexane and dried *in vacuo*, yield 18.09 mg (60.7%, based on unrecovered starting material), 81–83° dec (yellow-orange), 165–185° dec (orange-black). *Anal.* Calcd for C₈H₁₃OPtCl:

C, 24.8; H, 3.38; Pt, 50.7. Found: C, 24.4; H, 3.54; Pt, 51.5. Infrared spectrum (KBr pellet, Beckman IR-8): 3230 m, 3040 w, 2970 w, 2930 w, 1560 s, 1530 s, 1425 m, 1385 s, 1362 s, 1278 m, 1218 m, 1200 m, 1028 m, 982 w, 953 m, 935 w, 858 w, 828 m, 780 m, 702 w, 671 w, 643 m cm⁻¹. Proton nmr spectrum (Varian T-60, in CDCl₃): 1.88 (3 Hₐ, s), 2.02 (3 Hᵦ, s), 2.03 (3 Hᵨ, s), 3.96 (2 H_d, s), 5.42 (1 H_f, s) ppm. Each singlet was accompanied by ¹⁹⁵Pt satellites and the observed ¹⁹⁵Pt–H coupling constants were ∼6, 44, <5, 78, and 8 Hz, respectively.

(π-C₂H₃O)(PPh₃)₂PtCl, Preparation of. A dry benzene solution of Pt(Ph₃)₄, 0.97 g (0.84 mmol) in 10 ml of solvent, was treated with 2.5 mmol of ClCH₂CHO and 2 ml of dry methylene chloride 1.25 *M* in chloroacetaldehyde. After 30 min at room temperature 10 ml of 1:1 ether–heptane was added to the reaction mixture, and the white crystalline product was filtered off, yield 0.57 g (85%), mp 218–220°. *Anal.* Calcd for C₃₈H₃₃OP₂PtCl: C, 57.18; H, 4.17; P, 7.76; Cl, 4.44. Found: C, 57.07; H, 4.20; P, 7.75; Cl, 4.68. Infrared spectrum (KBr pellet, Beckman IR-8): 3090 m, 2970 w, 2820 w, 2720 w, 1650 s, 1480 m, 1430 s, 1380 w, 1330 w, 1308 w, 1183 w, 1158 w, 1140 m, 1090 s, 1025 w, 998 m, 847 w, 755 m, 742 s, 699 s, 690 s cm⁻¹. Proton nmr spectrum (Varian HA-100, in CDCl₃): The methylene protons (Hₐ) appeared as a seven-line multiplet at 2.76 ppm with ¹⁹⁵Pt satellites, the phenyl protons appeared between 7.0 and 7.6 ppm, and the aldehydic proton (Hᵦ) appeared as a triplet at 9.93 ppm with ¹⁹⁵Pt satellites. The observed coupling constants were $J_{P-H_a(trans)} = 11.0$, $J_{P-H_a(cis)} = 6.2$, $J_{Pt-H_a} = 70$, $J_{Pt-H_b} = 16$, and $J_{H_a-H_b} = 4.7$ Hz.

(π-C₂H₃)(PPh₃)PtCl, Attempted Conversion to (π-C₂H₃OH)-(PPh₃)₂PtCl. A 20-mg sample of the β-oxoethyl complex was dissolved in 0.5 ml of CDCl₃ and the nmr spectrum was observed as 1 equiv of dry HCl gas was added in aliquots at 25°. The signals of the β-oxoethyl group were progressively replaced by the doublet-quartet pattern of acetaldehyde, and a white precipitate of Pt-(PPh₃)₂Cl₂ formed.

K[(σ-acac)(acac)PtCl] and (π-acac)(acac)PtCl, Preparation of. These complexes were prepared *via* the procedures described by Holloway, Hulley, Johnson, and Lewis.[8]

Structure of *trans*-Chlorobis(triethylphosphine)-(*p*-fluorophenyldiazene)platinum(II) Perchlorate

Steven D. Ittel and James A. Ibers*

Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60201. Received December 26, 1973

Abstract: The structure of the title compound [Pt(P(C₂H₅)₃)₂(HNNC₆H₄F)Cl][ClO₄] has been determined at room temperature from three-dimensional X-ray data collected by counter methods. The structure has been refined by least-squares techniques to a final *R* index (on *F*) of 0.052 based on 4292 observations above background. The material crystallizes in the triclinic space group C_i^1-P1̄ with two molecules in a cell of dimensions $a = 9.167$ (2) Å, $b = 16.983$ (3) Å, $c = 8.947$ (2) Å, $\alpha = 91.46$ (1)°, $\beta = 96.34$ (1)°, and $\gamma = 77.04$ (1)°. The platinum atom has square-planar coordination. The cis diazene moiety lies in a plane roughly perpendicular to the coordination plane and its phenyl group is twisted to relieve steric interaction with the diazene proton. The diazene proton, which was refined, also has a close contact with the perchlorate anion. This compound, formed by protonation of an aryldiazonium complex of platinum, is the first aryldiazene complex to be structurally characterized and is an intermediate in a proposed model system for nitrogen fixation.

Transition metal complexes of aryldiazoniums can exist in three modes of coordination, the predominate canonical forms of which are shown in Figure 1. Several complexes of the singly bent diazenido (type B) have been characterized structurally.[1–4] (The

nomenclature used throughout this paper is based on the system proposed by Huang and Kosower[5] for

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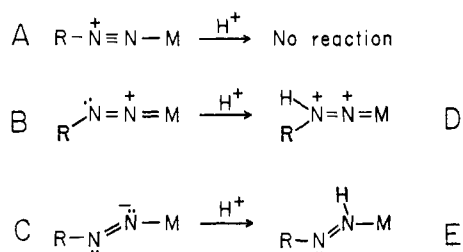(5) P. C. Huang and E. M. Kosower, *J. Amer. Chem. Soc.*, 90, 2362 (1968).

Figure 1. Transition metal complexes of aryldiazoniums and their protonated forms.

Figure 2. The mechanism of conversion between aryldiazenido, aryldiazene, and arylhydrazine complexes of platinum.

polynitrogen chain compounds. It has been extended to include complexes of those compounds.[6] Recently the first structure of a doubly bent diazenido (type C) complex was reported.[7] These structures are interesting because they show, in a close analogy with nitrosyl systems, that complexes of aryldiazoniums may exhibit an amphoteric nature. The complexes may be divided into two major classes, RN_2^+ and RN_2^-, represented by types B and C, respectively. On the basis of N–N stretching frequencies,[7] RN_2^+ may be subdivided with type A being a limiting case of type B in which the N–N bond approaches a triple bond.

On the basis of this division into three classes, protonation of the coordinated diazoniums may be characterized. Type A compounds should exhibit no reaction. Type B compounds may be protonated at N(2) to yield type D complexes which may formally be regarded as complexes of N-phenyl-N'-hydrazide(2 −). A structure of a type D complex of rhenium has recently been reported.[8] The doubly bent aryldiazenido complexes of type C should readily undergo attack at N(1) yielding 1,2-aryldiazene complexes of type E. This type of complex, first reported by Parshall,[9] has now been observed in a variety of systems.[4] Reactions of the diazenido complexes with a variety of cations other than H^+ result in complexes of disubstituted diazenes.

Parshall has characterized the platinum system illustrated in Figure 2 as "an inorganic analog of nitrogen reductase."[9b] The successive addition of hydrogen and concomitant reduction of N–N bond order of a coordinated aryldiazonium eventually to yield aniline and ammonia parallel a proposed[10] biological nitrogen fixation mechanism involving coordination of dinitrogen.

As part of a continuing study of the coordination of diazenes to transition metals,[11–14] it was felt that the structure of II would be of interest. It is one of the few known diazene complexes in which the diazene is presumably bound only through one nitrogen lone pair of electrons. Because free aryldiazenes are unknown,

it also presents another example of the stabilization of an unstable molecule through coordination to a transition metal (but phenyldiazene has been prepared from a copper complex as a very dilute acetonitrile solution).[15] The structures of I and III are currently under investigation.

Experimental Section

Preparation and Characterization. The compound [Pt(PEt$_3$)$_2$-(HNNC$_6$H$_4$F)Cl][BF$_4$], where Et = C$_2$H$_5$, was prepared by literature methods.[9] After conversion to Pt(PEt$_3$)$_2$(NNC$_6$H$_4$F)Cl it was reprotonated in diethyl ether with perchloric acid. The ether solution was allowed to evaporate over a period of 2 hr yielding large dark yellow crystals of [Pt(PEt$_3$)$_2$(HNNC$_6$H$_4$F)Cl][ClO$_4$]. The compound [Pt(PEt$_3$)$_2$(HNNPh)Cl][PF$_6$] (where Ph = C$_6$H$_5$) was prepared in a similar manner and its infrared spectrum was recorded on a Beckman IR-9 spectrometer. The (H^{15}N^{14}NPh) analog was prepared using ^{15}N enriched NaNO$_2$ (Stohler Isotope Chemicals) and its infrared spectrum was also recorded. These spectra, presented in Figure 3,[16] were identical throughout the entire spectrum indicating that the N=N stretch was not observed. Raman spectra were recorded using a Spex 1401 monochromator, a spinning sample technique, and 6471 Å Kr$^+$ ion laser excitation. The peak at 1506 cm^{-1} was shifted to 1484 cm^{-1} upon ^{15}N substitution indicating that it corresponds to the N=N stretching mode. A smaller peak at 1420 cm^{-1} was shifted to 1416 cm^{-1} indicating that it might arise from the N—C stretch which is influenced by the ^{15}N=N—C substitution.

Crystallographic Data. The crystals of [Pt(PEt$_3$)$_2$(HNNC$_6$H$_4$F)-Cl][ClO$_4$] display from 8 to 12 faces and a morphology consistent with the triclinic system. Precession photographs using Cu Kα radiation show only a center of inversion, indicating that the crystals indeed belong to the triclinic system.

Intensity measurements were made on two crystals mounted in argon filled capillaries with a Picker FACS-I computer-controlled four-circle X-ray diffractometer equipped with a scintillation counter and pulse height analyzer. The two crystals had approximate dimension of 0.6, 0.3, and 0.5 and 0.6, 0.4, and 0.4 mm, respectively. Cell constants and their standard deviations for the two crystals were derived from a least-squares refinement of the setting angles of 30 and 12 reflections, respectively, which had been centered on the Cu Kα_1 peak, λ 1.54056 Å, using a narrow source. The unit cell parameters for the first crystal are a = 9.167 (2) Å, b = 16.983 (3) Å, c = 8.947 (2) Å, α = 91.46 (1)°, β = 96.34 (1)°, γ = 77.04 (1)°, V = 1349.1 Å^3 (reduced cell). Those of the second crystal, which had larger deviations, agree within three standard deviations. The density calculated for two molecules per unit cell is 1.61 g/cm^3 which agrees with the experimental value of 1.58 (2) g/cm^3 measured by flotation in methyl bromide–dichloromethane.

The mosaicities of the crystals were measured by means of a narrow source, open-counter ω-scan technique and were found to be acceptable. Intensities were measured by the θ–2θ scan technique using nickel filtered Cu radiation. The takeoff angle of 3.0° for both crystals resulted in the intensity of a reflection being about 80% of its maximum value as a function of takeoff angle. Peaks were measured in 2θ from 0.8° below the Cu Kα_1 peak to 0.8° above the Cu Kα_2 peak, with 10-sec backgrounds measured at each

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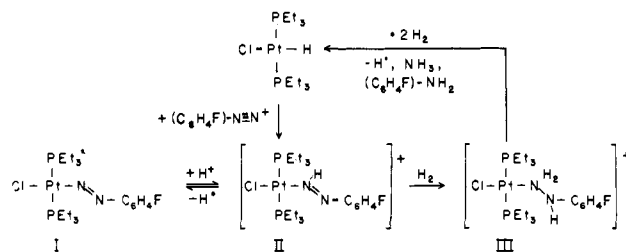(14) S. D. Ittel and J. A. Ibers, *Inorg. Chem.*, **12**, 2290 (1973).

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Table I. Positional and Thermal Parameters for Atoms of $[Pt(PEt_3)_2(HNNC_6H_4F)Cl][ClO_4]$

Atom	x^a	y	z	β_{11} or B^b	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pt	−0.03840 (4)	0.18118 (2)	−0.23749 (4)	96.2 (7)	30.6 (2)	122.2 (7)	−14.4 (2)	14.1 (3)	−5.0 (2)
P(1)	−0.2649 (2)	0.2566 (1)	−0.1704 (2)	101 (3)	40 (1)	140 (3)	−19 (1)	20 (2)	−5 (1)
P(2)	0.1909 (2)	0.1023 (1)	−0.2945 (2)	106 (3)	36 (1)	148 (3)	−10 (1)	15 (2)	−5 (1)
Cl(1)	−0.1389 (3)	0.0701 (1)	−0.2212 (4)	185 (4)	38 (1)	311 (6)	−37 (1)	76 (4)	−12 (2)
Cl(2)	0.2468 (3)	0.3318 (2)	0.1016 (3)	172 (4)	72 (1)	143 (3)	−42 (2)	13 (3)	−16 (2)
O(1)	0.3079 (9)	0.3069 (6)	−0.0378 (9)	176 (12)	90 (5)	170 (11)	−18 (6)	47 (9)	−25 (6)
O(2)	0.2586 (16)	0.4096 (8)	0.1379 (14)	564 (33)	104 (7)	334 (23)	−166 (13)	137 (22)	−84 (11)
O(3)	0.0925 (10)	0.3299 (7)	0.0768 (11)	170 (14)	114 (6)	238 (15)	−62 (8)	70 (11)	−40 (8)
O(4)	0.3177 (14)	0.2787 (9)	0.2174 (12)	328 (22)	128 (9)	212 (16)	−19 (11)	−48 (15)	31 (10)
N(1)	0.0412 (8)	0.2793 (4)	−0.2495 (8)	124 (10)	28 (2)	141 (9)	−11 (4)	18 (8)	2 (4)
N(2)	0.0602 (10)	0.3106 (5)	−0.3669 (9)	191 (13)	43 (3)	134 (10)	−24 (5)	35 (9)	−2 (4)
C(7)	−0.2687 (12)	0.3647 (6)	−0.1553 (14)	136 (14)	39 (4)	266 (20)	−14 (6)	63 (13)	−32 (7)
C(8)	−0.4160 (16)	0.4166 (8)	−0.1139 (23)	199 (21)	48 (5)	478 (43)	−19 (8)	137 (25)	−58 (12)
C(9)	−0.4213 (11)	0.2481 (6)	−0.3054 (13)	122 (13)	40 (4)	212 (16)	−22 (5)	5 (11)	−8 (6)
C(10)	−0.4086 (15)	0.2761 (8)	−0.4627 (13)	200 (21)	66 (5)	171 (15)	−21 (8)	−15 (14)	1 (7)
C(11)	−0.3107 (13)	0.2244 (8)	0.0081 (12)	166 (17)	73 (6)	173 (15)	−28 (8)	82 (13)	−1 (7)
C(12)	−0.1870 (19)	0.2244 (11)	0.1321 (15)	258 (28)	113 (10)	166 (17)	−46 (14)	28 (18)	6 (11)
C(13)	0.3356 (12)	0.1069 (7)	−0.1415 (13)	137 (15)	55 (5)	198 (16)	−9 (7)	−12 (12)	−8 (7)
C(14)	0.2983 (18)	0.0783 (12)	0.0069 (17)	252 (26)	120 (11)	186 (21)	−1 (14)	−32 (18)	31 (12)
C(15)	0.1954 (13)	−0.0035 (6)	−0.3318 (14)	193 (17)	35 (3)	237 (19)	−15 (6)	42 (14)	−25 (6)
C(16)	0.3485 (17)	−0.0561 (8)	−0.3635 (21)	208 (24)	52 (5)	379 (36)	5 (9)	29 (23)	−43 (11)
C(17)	0.2582 (14)	0.1369 (7)	−0.4582 (13)	190 (18)	47 (4)	202 (17)	−8 (7)	81 (14)	−9 (7)
C(18)	0.1478 (20)	0.1403 (9)	−0.5974 (14)	377 (35)	65 (7)	158 (16)	−32 (12)	32 (19)	−6 (8)
F	0.2699 (12)	0.5858 (6)	−0.3875 (12)	10.7 (3)					
C(1)	0.1108 (11)	0.3833 (5)	−0.3613 (10)	4.6 (2)					
C(2)	0.0840 (12)	0.4407 (6)	−0.2452 (12)	5.3 (2)					
C(3)	0.1362 (13)	0.5100 (7)	−0.2593 (13)	6.0 (2)					
C(4)	0.2158 (15)	0.5160 (8)	−0.3788 (15)	6.7 (3)					
C(5)	0.2381 (16)	0.4636 (8)	−0.4918 (16)	7.0 (3)					
C(6)	0.1837 (13)	0.3956 (7)	−0.4818 (13)	5.8 (2)					
H(N1)	0.037 (10)	0.332 (6)	−0.170 (11)	4.3					

^{a} Numbers in parentheses here and throughout the paper are estimated standard deviations in the least significant digits. ^{b} The form of the anisotropic thermal ellipsoid is $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}kl)$. The values of β have been multiplied by 10^4.
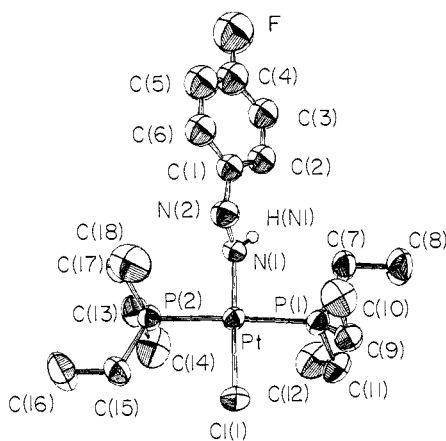

Figure 4. A drawing of the $[Pt(PEt_3)_2(HNNC_6H_4F)Cl]^+$ cation with most H atoms omitted for the sake of clarity. The vibrational ellipsoids are drawn at the 50% probability level.

end of the scan. The counter was positioned 30 cm from the crystal and was preceded by an aperture of 5×5 mm. The pulse height analyzer was set to admit 90% of the Cu $K\alpha$ peak, and copper foil attenuators were automatically inserted if the intensity of the diffracted beam exceeded about 7000 counts/sec during the scan. All reflections were scanned at 2°/min.

The intensities of six standard reflections were measured after every 100 reflections. Data collection was terminated on the first crystal at $2\theta = 100°$ after two of the standards had fallen to 80% of their initial intensities. Two of the other standards showed a slight drop off while the remaining two were constant. The second crystal was used to collect data from $2\theta = 98$ to 125° in the normal bisecting mode and then from $2\theta = 123$ to 155° in the parallel mode. Decomposition in the second crystal was not as great as in the first, but it was again anisotropic. Because of its anisotropic nature, no correction for decomposition was made.

Solution and Refinement of the Structure. All data were pro-

cessed as described previously;[17] a value of 0.04 was used for p in the estimation of $\sigma(F_o^2)$. After rejecting overlapping data a total of 4292 unique reflections obeying the condition $F_o^2 > 3\sigma(F_o^2)$ was obtained. Only these reflections were used in subsequent calculations.

The structure was solved using a Patterson synthesis.[18] Using the data from the first crystal, it was possible to locate the Pt, P, and Cl positions. Two cycles of refinement using the 1000 inner data, each followed by a difference Fourier synthesis, led to positions for all non-hydrogen atoms. Refinement of the structure was carried out by full-matrix least-squares techniques. Throughout the refinement, the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes, and the weight, w, is $4F_o^2/\sigma^2(F_o^2)$. The agreement indices R and R_w are defined as

$$R = \sum(|F_o| - |F_c|)/\sum|F_o|$$

and

$$R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$$

The atomic scattering factors for nonhydrogen atoms were from the tabulation in ref 19; the values for hydrogen were those of Stewart, et al.[20] The anomalous dispersion terms of Cromer[21] for Pt, P, Cl; and F were applied to the calculated structure factors. A further cycle of refinement in which the phenyl ring was constrained to a rigid group[22] with C–C bond distances of 1.397 Å and D_{6h} symmetry and all non-hydrogen atoms were assigned isotropic thermal

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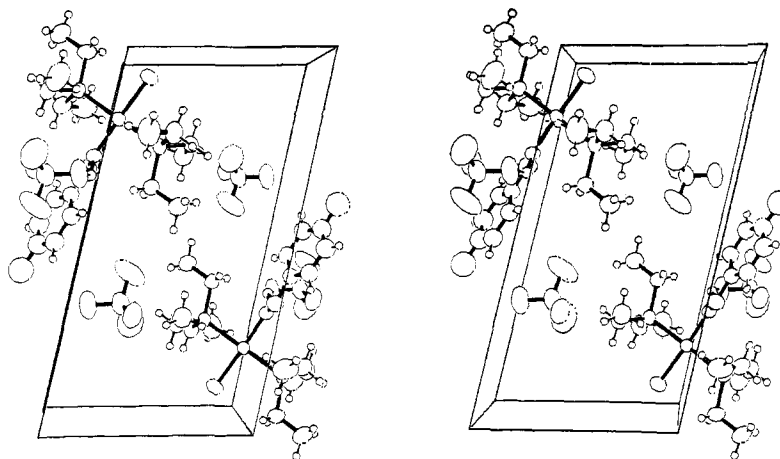(22) S. J. La Placa and J. A. Ibers, *Acta Crystallogr.*, 18, 511 (1965).

Figure 5. A stereo view of the unit cell of [Pt(PEt₃)₂(HNNC₆H₄F)Cl][ClO₄]. The fixed hydrogen atoms have been assigned temperature factors of 1.0 Å² for the sake of clarity. Two extra perchlorate ions are drawn to illustrate the O(3)–H(N1) interaction. The x axis goes to the right, the y axis is vertical, and the z axis is toward the reader.

parameters led to values of R and R_w of 0.116 and 0.155, respectively.

At this point, the data from the second crystal had been collected. All observed intensities were corrected for absorption using an analytical method. The well-formed crystals permitted accurate measurement of the crystal dimensions using a micrometer eyepiece, and thus an accurate description of the crystal shape. Calculated transmission factors ranged from 0.052 to 0.142, based on $\mu = 121.8$ cm⁻¹. A further cycle of refinement using the combined data set resulted in agreement factors of 0.085 and 0.111 for R and R_w, respectively. Two further cycles of refinement in which the rigid group approximation was dropped and all non-phenyl atoms of the complex were allowed to vibrate anisotropically resulted in agreement factors of 0.061 and 0.080. Difference Fourier syntheses resulted in reasonable positions for all methyl hydrogen atoms. These positions and those of the methylene hydrogen atoms were idealized assuming tetrahedral geometry and C–H distances of 1.00 Å. The phenyl hydrogen atom positions were idealized assuming planar trigonal geometry. The hydrogen atoms were assigned isotropic thermal parameters equal to the values of the atoms to which they were attached. A fixed contribution from these hydrogen atoms was added to all subsequent structure factor calculations.

A cycle of refinement in which the atoms of the perchlorate anion were allowed to vibrate anisotropically led to values of 0.055 and 0.071 for R and R_w. A difference Fourier synthesis revealed a reasonable position for H(N1). This hydrogen was assigned a temperature factor equal to the last isotropic temperature factor of N(1), and its positional coordinates were varied in two final full cycles of refinement. The final values of R and R_w were 0.052 and 0.066 for 4292 observations and 241 variables.

An analysis of $\Sigma w(|F_o| - |F_c|)^2$ as a function of scattering angle, $|F_o|$, and Miller indices revealed no unexpected trends. The error in an observation of unit weight is 2.66 electrons. The maximum density on a final difference Fourier synthesis was a residual of 1.49 e/Å³ near Pt. This may be compared with a peak of 0.43 e/Å³ assigned to the diazene hydrogen atom at a final stage of refinement.

The final atomic positional and thermal parameters along with their standard deviations as estimated from the inverse matrix are given in Table I. Table II lists the idealized positional coordinates for the hydrogen atoms together with their assigned thermal parameters.[16] The final values of $10|F_o|$ and $10|F_c|$ in electrons are given in Table III;[16] only the reflections which were used in the refinement are listed in this table. Table IV presents the root-mean-square amplitudes of vibration.[16]

Description of the Structure and Discussion

The structure consists of the packing of monomolecular units. The perchlorate anion is ordered and well behaved. Figure 4 presents the labeling scheme for the complex and Figure 5 presents a stereoscopic view of the packing. Hydrogen atoms bear the same num-

bers as the carbon atoms to which they are attached, with suffixes to distinguish between the three methyl and two methylene hydrogen atoms. The shortest intermolecular contact is 2.21 (10) Å between H(N1) and O(3) of the perchlorate. Selected interatomic distances and angles are presented in Table V. Table VI presents data on selected dihedral angles[13,23] and Table VII presents deviations from selected planes.

The complex is square planar as indicated by the small deviations from Plane 1 in Table VII. The Pt–P bond distances of 2.314 (2) Å for P(1) and 2.326 (2) Å for P(2) are normal for trans trialkylphosphines.[24] The P(2) distance is lengthened slightly, perhaps because of an interaction of the hydrogen atoms on C(15) with Cl(1). This interaction is reflected in the bond angles of 92.2 (1)° for P(2)–Pt–Cl(1) and 86.6 (1)° for P(1)–Pt–Cl(1). It is also reflected in the Pt–P–C angles which are equal around P(1) but unequal around P(2) in a manner that moves C(15) away from Cl(1).

The Pt–Cl(1) distance of 2.291 (2) Å is short (see Table VIII) indicating that the trans diazene has a very small trans influence.[24–28] This small trans influence implies that π bonding is of little importance in the bonding of the diazene to the platinum. This result, not unexpected in spite of the fact that it has been shown that diazenes are capable of forming strong π bonds,[12,13] is supported by the infrared spectral data. The N=N stretching frequency of 1506 cm⁻¹ is very similar to those of other aryldiazene complexes. Cationic complexes and complexes with a variety of π bonding ligands all[29] have N=N stretches in a very narrow range[4] around 1510 cm⁻¹, indicating that the N=N bond depends very little on the ability of the metal to supply electrons for π back-bonding.

The Pt–N(1) bond length, 1.973 (7) Å, is that which

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(29) An exception is a copper diazene complex (C₆H₅N–NH)Cu₃Cl₄, in which the diazene is presumed to be bridging: D. Petredis, A. Burke, and A. L. Balch, *J. Amer. Chem. Soc.*, **92**, 428 (1970).

Table V. Selected Distances (Å) and Bond Angles (deg) in [Pt(PEt₃)₂(HNNC₆H₄F)Cl][ClO₄]

Bond distances		Bond angles	
Pt–P(1)	2.314 (2)	P(1)–Pt–Cl(1)	86.6 (1)
Pt–P(2)	2.326 (2)	P(2)–Pt–Cl(1)	92.2 (1)
Av	2.320 (6)^a	P(1)–Pt–N(1)	91.3 (2)
		P(2)–Pt–N(1)	89.9 (2)
Pt–Cl(1)	2.291 (2)	Pt N(1)–N(2)	125.3 (6)
Pt–N(1)	1.973 (7)	Pt–N(1)–H(N1)	130 (4)
N(1)–N(2)	1.235 (10)	N(2)–N(1)–H(N1)	100 (5)
N(1)–H(N1)	1.12 (10)	N(1)–H(N1)–O(3)	128 (6)
N(2)–C(1)	1.410 (12)	N(1)–N(2)–C(1)	120.0 (8)
C(4)–F	1.391 (16)	N(2)–C(1)–C(2)	123.3 (9)
		N(2)–C(1)–C(6)	114.6 (9)
C(1)–C(2)	1.410 (13)	C(6)–C(1)–C(2)	122.1 (10)
C(1)–C(6)	1.374 (14)	C(1)–C(2)–C(3)	116.0 (10)
C(2)–C(3)	1.379 (16)	C(1)–C(6)–C(5)	121.0 (11)
C(6)–C(5)	1.365 (18)	C(2)–C(3)–C(4)	118.5 (11)
C(3)–C(4)	1.377 (17)	C(6)–C(5)–C(4)	116.0 (13)
C(5)–C(4)	1.332 (18)	C(3)–C(4)–C(5)	126.1 (13)
		C(3)–C(4)–F	117.0 (12)
Av	1.373 (18)	C(5)–C(4)–F	116.8 (13)
P(1)–C(7)	1.830 (10)	Pt–P(1)–C(7)	112.8 (3)
P(1)–C(9)	1.800 (10)	Pt–P(1)–C(9)	112.3 (3)
P(1)–C(11)	1.823 (10)	Pt–P(1)–C(11)	112.5 (4)
P(2)–C(13)	1.811 (11)	Pt–P(2)–C(13)	109.8 (4)
P(2)–C(15)	1.812 (10)	Pt–P(2)–C(15)	116.1 (4)
P(2)–C(17)	1.811 (11)	Pt–P(2)–C(17)	113.5 (4)
Av	1.815 (11)	Nonbonded distances	
		H(N-1)–H(2)	1.71
C(7)–C(8)	1.516 (15)	N(1)–C(2)	2.853 (13)
C(9)–C(10)	1.521 (16)	N(1)–O(3)	3.038 (12)
C(11)–C(12)	1.496 (18)	H(N1)–C(7)	2.75 (9)
C(13)–C(14)	1.524 (19)	H(N1)–O(3)	2.21 (10)
C(15)–C(16)	1.536 (17)	Cl(1)–P(1)	3.158 (3)
C(17)–C(18)	1.510 (19)	Cl(1)–P(2)	3.326 (4)
		N(1)–P(1)	3.076 (8)
Av	1.517 (19)	N(1)–P(2)	3.048 (7)
Cl(2)–O(1)	1.439 (8)		
Cl(2)–O(2)	1.379 (11)		
Cl(2)–O(3)	1.414 (9)		
Cl(2)–O(4)	1.395 (11)		
Av	1.407 (23)		

^{a} For the averaged quantities, the estimated standard deviation is the larger of an individual standard deviation or the standard deviation of a single observation as calculated from the mean.

Table VI. Selected Interplanar and Vector Plane-Normal Angles^a (deg) in [Pt(PEt₃)₂(HNNC₆H₄F)Cl][ClO₄]

Dihedral		Vector plane-normal	
Pt–N(1)–N(2) N(1)–N(2)–H(N1)	159 (5)	N(1)–N(2) P(1)–P(2)–N(1)	140.4 (6)
Pt–N(1)–N(2) N(1)–N(2)–C(1)	176.7 (6)	N(1)–H(N1) Pt–N(1)–N(2)	70 (5)
Pt–N(1)–N(2) C(1)–C(3)–C(5)	−28.7 (9)		
Pt–N(1)–N(2) P(1)–N(1)–P(2)	73.8 (7)		
N(1)–N(2)–C(1) H(N1)–N(1)–N(2)	17 (5)		
C(1)–N(2)–N(1) C(1)–C(3)–C(5)	26.7 (9)		
N(1)–N(2)–C(1) P(1)–P(2)–N(1)	71.8 (8)		

^{a} For a definition of the angles see ref 13 or 23.

would be expected for an sp² hybridized nitrogen atom. The Cl atom exerts little trans influence. The N(1)–N(2) double bond length of 1.235 (10) Å is in good agreement with that of free azobenzene,[30] 1.24 (3) Å.

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Table VII. Deviations (Å) from Weighted Least-Squares Planes of Atoms Used to Determine the Planes^a

	1	2	3	4
Pt	−0.0018 (3)	0.0000 (3)		
P(1)	0.044 (2)			
P(2)	0.045 (2)			
Cl(1)	−0.002 (4)			
N(1)	0.001 (7)	0.021 (7)		
N(2)		0.025 (9)	0.001 (9)	
H(N1)		−0.36(9)		
C(1)		−0.029 (9)	0.014 (9)	0.010 (9)
C(2)			0.004 (11)	0.003 (11)
C(3)			−0.031 (12)	−0.023 (11)
C(4)			0.017 (13)	0.029 (13)
C(5)			−0.015 (14)	−0.006 (14)
C(6)			−0.017 (12)	−0.016 (12)
F			0.013 (11)	

Plane	A	B	C	D
1	2.073	−0.641	8.402	−2.189
2	7.616	−6.015	−0.406	−1.285
3	6.688	−4.767	3.815	−2.479
4	6.722	−4.671	3.804	−2.430

^{a} Plane equation: $Ax + By + Cz - D = 0$ with x, y, and z in triclinic coordinates.

Table VIII. Platinum–Chlorine Bond Lengths in Some Square Planar Platinum(II) Complexes

Molecule	Trans ligand	Pt–Cl (Å)	Ref
cis-Pt(C₁₄H₂₁N)Cl₂	R₂HC	2.430 (2)	25
trans-Pt(PPh₂Et)₂HCl	H	2.422 (9)	26
cis-Pt(PMe₃)₂Cl₂	R₃P	2.376 (12)	27
cis-Pt(C₁₄H₂₁N)Cl₂	C=C	2.334 (3)	25
[Pt(NH₃)Cl₃]⁺	N(sp³)	2.317 (7)	24
trans-Pt(PEt₃)₂Cl₂	Cl	2.291 (2)	This work
[*trans*-Pt(PEt₃)₂-(HNNC₆H₄F)Cl]⁺	N(sp²)		
[Pt(NH₃)Cl₃]⁺	Cl	2.280 (14)	28

Comparison of the N(1)–N(2) bond length with the 1.17 (2) Å found in the rhodium diazenido complex,[5] [Rh-(PhP((CH₂)₃PPh₂)₂)Cl(N₂Ph)][PF₆], indicates that protonation possibly decreases the N–N bond order. This effect is also found in the protonation of a phenyldiazenido complex to yield a complex of a N-phenyl-N'-hydrazide(2−).[8]

The N(2)–C(1) bond length, 1.410 (12) Å, is comparable with that found in free azobenzene and in the Rh–diazenido complex. The plane defined by Pt–N(1)–N(2) makes an angle of 73.8 (7)° to the coordination plane as defined by P(1)–N(1)–P(2).

The bond lengths and angles around the phenyl ring deviate from the expected D_{6h} symmetry. Planes 3 and 4 in Table VII point out a slight lack of planarity. This apparent distortion probably results from the libration of the entire phenyl ring as the bond lengths tend to get shorter as one moves out on the ring away from the nitrogen atom. There is no evidence of any quinoidal nature in the phenyl ring.

The plane of the phenyl ring, as described by C(1)–C(3)–C(5), makes an angle of 26.7 (9)° with the C(1)–N(2)–N(1) plane to increase the H(2)–H(N1) close contact to 1.71 Å. If this twist about the N(2)–C(1) bond were 0° and all other parameters were unchanged, the H(2)–H(N1) contact would be 1.5 Å. This twist, which should be 0° for the optimum conjugation be-

tween the ring and the N=N double bond, has been observed in both free[30] and complexed azobenzene.[12] These trans diazenes displayed twist angles up to 17.1°. The structure of cis-azobenzene[31] displays a twist angle of 34° because of the steric interaction of the two phenyl rings. The attempt to relieve the H(2)–H(N1) close contact is also reflected in the N(1)–C(1)–C(2) and N(1)–C(1)–C(6) bond angles which are 123.3 (9) and 114.6 (9)°, respectively.

The nitrogen–hydrogen bond, N(1)–H(N1), of 1.12 (10) Å is normal. The N(1)–O(3) distance suggests a potential interaction, but the N(1)–H(N1)–O(3) angle of 128 (6)° precludes description of this interaction as a hydrogen bond.

It is clear that the complexation, two-electron reduction, and protonation of an aryldiazonium cation has reduced the N–N bond order from a triple bond to a double bond. The resulting aryldiazene complex represents a model for the intermediate diazene complex in the proposed mechanism for biological nitrogen

fixation. Further reduction of the N–N bond order would eventually lead to the desired cleavage of the N–N bond. Though this model is appealing because it does not necessitate any unusual separation of charge, the 1,1-diazene complex found in the rhenium system[8] cannot be ruled out as a model nor can the symmetrical, π-bonded type of 1,2-diazene complex found in several Ni(0) systems.[12,13]

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Tetraphenylporphinecobalt(II) Complexes as a Probe for the Nature of Phosphine σ-Donor Orbitals. Electron Paramagnetic Resonance Studies of Phosphine and Dioxygen Complexes

B. B. Wayland* and M. E. Abd-Elmageed

Contribution from the E. F. Smith Laboratory of Chemistry and the Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19174. Received January 29, 1974

Abstract: Tetraphenylporphinecobalt(II) forms 1:1 complexes with trivalent phosphorus ligands. All of the 1:1 complexes have effective axial symmetry with a $(d_{xz}, d_{yz}, d_{xy})^6(d_{z^2})^1$ ground configuration. Cobalt-59 and phosphorus-31 hyperfine coupling constants are utilized in evaluating the odd electron spin distribution and the phosphorus 3s and 3p character in the coordinated phosphine σ-donor orbital. The 3s character in the coordinated phosphorus σ-donor orbital is found to increase substantially with increased electron withdrawing ability of the substituents. Phosphorus ligand spin densities are found to decrease as the donor orbital P_{3s} character increases. Properties of the M–P σ bonding are discussed and compared with results on the corresponding CO, CH_3NC, and C_5H_5N complexes. Dioxygen complexes $(Co^{II}TPP \cdot PX_3 \cdot O_2)$ which exhibit ^{31}P hyperfine coupling are reported and discussed.

Descriptions of the bonding of trivalent phosphorus ligands with metallo species have resulted in controversies centered on the relative importance of σ-donor and π-acceptor effects on observed properties such as metal–phosphorus (M–P) bond distances,[1,2] vibrational frequencies,[3–6] and ^{31}P nmr shifts and coupling constants.[7–10]

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A problem encountered in previous studies of metal–phosphorus bonding is that the observed properties do not definitively separate σ- and π-electronic effects. The only experiments which can clearly separate these effects involve observations that specifically probe the individual molecular orbitals involved in the σ and π bonding. Epr studies of metallophosphine complexes which have an odd electron isolated in either the σ or π molecular orbitals can provide this direct bonding probe.

This paper reports on epr studies for a series of 1:1 trivalent phosphorus ligand complexes of tetraphenylporphyrincobalt(II), [Co^{II}TPP], where the unpaired electron is principally confined in a cobalt–phosphorus σ molecular orbital. Cobalt-59 and phosphorus-31 hyperfine coupling constants are utilized in evaluating the odd electron spin distribution and the phosphorus 3s and 3p character in the ligand σ-donor orbital.