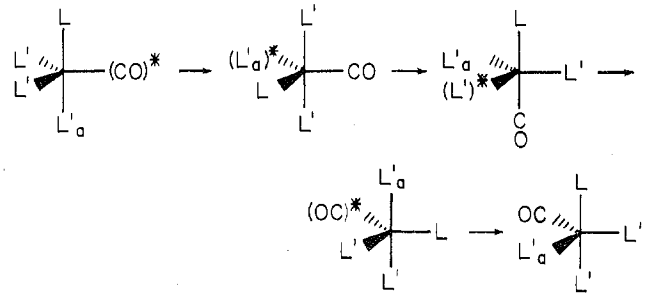
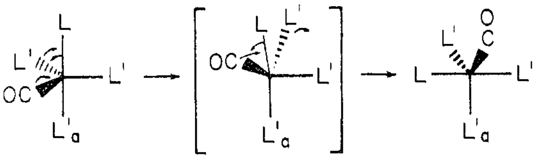
Scheme I



Scheme II



Although a specific sequence of four (!) Berry motions (Scheme I[19]) interchanges the axial phosphite with one equatorial phosphite, the "tetrahedral edge traverse" (Scheme II) does so in an apparently simpler fashion.[20]

The axial–equatorial coupling constant in $IrL'_5{}^+$ is 59 Hz. This is a coupling between two phosphite ligands. The similarity of this value to the axial–equatorial phosphite–phosphine coupling constants found here suggests that this parameter may fall in a narrow range which will be structurally diagnostic. The coupling constant measured here for IrL'_4L^+ is also similar, which indicates that an equatorial–equatorial J is also less than about 70 Hz. Finally, the trans coupling constant appears to be significantly larger.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. $Ir[P(OCH_2)_3CCH_3]_5Cl$, 55701-82-1; $Ir[P(OCH_2)_3CCH_3]_4(PPh_3)^+$, 55669-38-0; $Ir[P(OCH_2)_3CCH_3]_3(PPh_3)CO^+$, 55669-39-1; $Ir[P(OCH_2)_3CCH_3]_4CO^+$, 55669-40-4; $Ir[P(OCH_2)_3CCH_3]_3(PPh_3)_2{}^+$, 55669-41-5; $Ir[P(OCH_2)_3CCH_3]_2(PPh_3)_2CO^+$, 55669-42-6; $IrCOCl(PPh_3)_2$, 14871-41-1; $IrN_2Cl(PPh_3)_2$, 15695-36-0; ^{31}P, 7723-14-0.

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

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The reasons for our interest in diazonium complexes of Pt(II) have been detailed previously.[1,2] The present parent complex $PtCl(N_2C_6H_4F)(PEt_3)_2$, Et = C_2H_5, denoted I in ref 2, is part of a three-compound scheme proposed by Parshall[3] as an inorganic model for nitrogen fixation. The structures of the other compounds in the scheme, $PtCl(HNNC_6H_4F)(PEt_3)_2$[1] (II) and $PtCl(H_2NNHC_6H_4F)(PEt_3)_2$[2] (III), have been described. The structure of I, which has the doubly bent M—N=N—R configuration, is reported here.

Experimental Section

The title compound, I, was prepared by literature methods.[3c] Crystals suitable for X-ray study were obtained by slow evaporation of a hexane solution of the compound. Preliminary precession and Weissenberg photographs of these crystals indicated that the space group is either C_{2h}^6-$C2/c$ or C_s^4-Cc.

A well-formed crystal was chosen for data collection and sealed in a capillary under argon. Cell constants were determined by hand centering 15 high-order reflections on a Picker four-circle diffractometer using monochromatic Mo $K\alpha_1$ radiation (λ 0.70930 Å). The cell parameters are a = 9.320 (6), b = 20.244 (9), c = 12.826 (6) Å, β = 97.59 (1)°, and V = 2398.9 Å^3. The density of 1.63 g/cm^3 calculated on the basis of four molecules per unit cell agrees well with the observed value of 1.63 (2) g/cm^3 measured by flotation in an aqueous zinc chloride solution.

Intensity data were collected out to 2θ (Mo $K\alpha$) = 52° on a Picker FACS-1 computer controlled diffractometer using the θ–2θ scan technique. Six standard reflections, which were measured after every 100 reflections, declined by an average of 3% during the course of data collection. A correction for this decline was applied during data processing.

The 2881 measured reflections were processed in the usual manner with a value of 0.04 chosen for p.[4] The intensities were then corrected for absorption (μ = 61.6 cm^{-1}).[5] The resulting 2011 unique reflections obeying the condition $F_o{}^2 > 3\sigma(F_o{}^2)$ were used in all further calculations.

Solution and Refinement of the Structure

The structure was solved by means of a sharpened origin-removed Patterson synthesis,[5] which revealed the positions of the platinum, phosphorus, and chlorine atoms. The distribution of normalized structure factors indicated that the space group was noncentrosymmetric. Therefore, refinement was started in the space group Cc using full-matrix least-squares techniques. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes and the weights, w, are defined as $4F_o{}^2/\sigma^2(F_o{}^2)$. 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 first cycle of refinement with initial parameters from the Patterson synthesis resulted in values for R and R_w of 0.262 and 0.352, respectively.[6] A difference Fourier synthesis followed by two cycles of least-squares and difference Fourier syntheses led to refined positions for the phosphine carbon atoms and possible positions for the atoms of the p-fluorophenyldiazo moiety. But there was no well-defined electron density in the region where the nitrogen atoms were expected. Moreover, we were unable to refine coordinates for the carbon atoms of the phenyl ring, even when the ring was treated as a rigid group. These problems, along with the facts that the two triethylphosphine groups appeared to be related by a twofold rotation axis and that the Cl, Pt, C(1), C(4), and F atoms appeared to be collinear, indicated the correct space group was probably the centrosymmetric one, $C2/c$, in which a $C2$ axis is imposed upon the molecule. A second harmonic generation test failed to detect the absence of a center of symmetry.[7]

Refinement of the Pt, Cl, and phosphine moiety atom positions in space group $C2/c$ followed by a difference Fourier synthesis led to positions for the atoms of the fluorophenyl group. From the diffuse

TABLE I . POSITIONAL AND THERMAL PARAMETERS FOR THE ATOMS OF [PTCL(N2C6H4F)(PET3)2]

ATOM	X[A]	Y	Z	B11[B] OR B,A^2	B22	B33	B12	B13	B23
PT	0	0.13847(4)	1/4	13.28(13)	2.34(2)	4.16(5)	0	1.12(5)	0
CL	0	0.0193(3)	1/4	15.8(9)	2.69(15)	11.6(6)	0	2.2(6)	0
P	0.0074(5)	0.13594(20)	0.4301(3)	15.8(6)	2.86(11)	4.68(24)	0.05(21)	2.1(3)	0.61(13)
F	0.015(7)	0.5453(11)	0.2316(26)	41.(9)	4.5(6)	11.(3)	3.3(24)	6.(4)	5.4(13)
N(1)	0.037(3)	0.2345(14)	0.250(3)	3.3(7)					
N(2)	-0.0598(28)	0.2704(12)	0.2546(24)	12.(3)	1.8(6)	9.2(23)	1.5(11)	3.7(26)	0.C(9)
C(1)	-0.0307(28)	0.3428(10)	0.2527(27)	3.1(5)					
C(2)	0.101(5)	0.3670(20)	0.224(3)	4.5(7)					
C(3)	0.123(4)	0.4374(21)	0.221(3)	4.1(8)					
C(4)	0.004(15)	0.4729(14)	0.237(9)	5.4(9)					
C(5)	-0.109(6)	0.4549(26)	0.268(5)	6.4(13)					
C(6)	-0.139(5)	0.3853(22)	0.271(3)	5.0(9)					
C(7)	0.1439(22)	0.0796(10)	0.4931(16)	20.(3)	3.9(6)	8.2(15)	2.5(11)	1.1(17)	1.4(8)
C(8)	0.2969(25)	0.0976(13)	0.4777(18)	20.(4)	5.9(9)	9.4(18)	3.3(15)	0.5(20)	0.5(10)
C(9)	0.0387(23)	0.2150(9)	0.4967(14)	21.(3)	4.1(6)	4.7(11)	0.7(10)	1.4(15)	-0.9(6)
C(10)	0.047(3)	0.2141(12)	0.6164(15)	40.(6)	5.9(9)	3.9(12)	5.1(18)	1.1(21)	-0.9(8)
C(11)	-0.1630(26)	0.1049(10)	0.4665(17)	24.(4)	4.1(6)	9.6(17)	-1.1(12)	8.2(21)	1.1(8)
C(12)	-0.2874(26)	0.1461(13)	0.431(3)	13.4(29)	6.7(11)	18.(3)	-0.2(14)	4.6(26)	-0.6(14)

[A] ESTIMATED STANDARD DEVIATIONS IN THE LEAST SIGNIFICANT FIGURE(S) ARE GIVEN IN PARENTHESES IN THIS AND ALL SUBSEQUENT TABLES. [B] THE FORM OF THE ANISOTROPIC THERMAL ELLIPSOID IS: EXP(-(B11H^2+B22K^2+B33L^2+2B12HK+2B13HL+2B23KL)). THE QUANTITIES GIVEN IN THE TABLE ARE THE THERMAL COEFFICIENTS X 10^3.

peak in the area of the nitrogen atoms two atom positions, both on the symmetry axis, were postulated. Refinement of this ordered model led to an unreasonably short N(1)–N(2) bond length of 1.02 Å. Moreover, on chemical grounds[3,8] we expected a doubly bent metal–diazo structure. In addition, in this ordered model there was significant electron density off of the symmetry axis in the region of the nitrogen atoms and the thermal ellipsoids of the phenyl ring carbon atoms were elongated. This strongly indicates that the diazo moiety is doubly bent and the entire aryldiazo ligand is disordered. Several cycles of refinement were carried out on this disordered model, with the phenyl group refined as a rigid group. Anomalous scattering terms[6] were applied to the Pt, P, Cl, and F atoms, and all nongroup atoms were allowed to vibrate anisotropically. The positions of the ethyl and phenyl hydrogen atoms were idealized assuming tetrahedral or planar trigonal geometry and C–H distances of 1.0 Å and their contributions were added to the calculated structure factors.

In the final refinement all atoms were refined individually although it was found necessary to restrict the carbon atoms of the phenyl ring and N(1) to isotropic vibration. The final values of R and R_w are 0.085 and 0.101.

Table I lists the final positional and thermal values for the refined atoms. Idealized hydrogen atom parameters are given in Table II.[9] Table III lists the root-mean-square amplitudes of vibration.[9] Values of $10|F_o|$ and $10|F_c|$ are given in Table IV.[9]

Description of the Structure and Discussion

The geometry of the $PtCl(N_2C_6H_4F)(PEt_3)_2$ molecule and an atomic labeling scheme is shown in Figure 1. A crystallographically imposed twofold rotation axis passes through the molecule, coincident with the Pt–Cl vector. This axis relates the phosphine ligands and necessitates disorder in the aryldiazo group. The N(1), N(2), and F atoms are respectively 0.35, 0.57, and 0.29 Å away from the symmetry axis. The geometric center of the ring lies on the symmetry axis. The angle between the least-squares plane of the phenyl ring and the plane defined by atoms N(1), N(2), and C(1) is 12.7 (11)°. This angle, of course, is zero for maximum overlap of nitrogen and phenyl ring π orbitals.

Many structural features are clear despite the large standard deviations which presumably arise from our inability to treat the disorder thoroughly. The coordination about the Pt atom is essentially square planar with trans phosphine ligands as shown in Figure 1. The P–Pt–Cl and P–Pt–N(1) bond angles are 88.7 (1)° and 90.4 (12)°, respectively. The Pt–P bond length of 2.302 (4), although somewhat shorter than in II or III, is not unusual for trans phosphine ligands.

The Pt–N(1)–N(2) linkage in this compound is doubly bent, corresponding formally to coordination of ArN_2^-. The Pt–N(1)–N(2) and N(1)–N(2)–C(1) bond angles are respectively 118 (2)° and 117 (2)°. This mode of bonding is not unexpected. The reported value of ν(NN)[3b,10] falls in the range anticipated for a doubly bent aryldiazo group.[8] Also, protonation has previously been shown to occur only at N(1).[3a,1] This type of protonation is expected for a doubly bent structure where N(1) carries a formal negative charge. Recently there has been an example of protonation at N(2) in a singly bent aryldiazo moiety,[11] again an expected result.

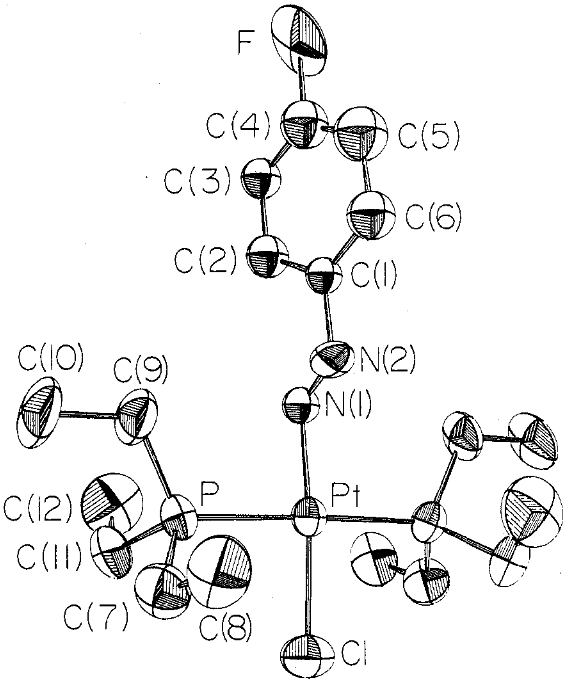
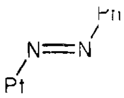
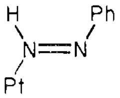
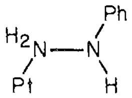


Figure 1. A drawing of the $PtCl(N_2C_6H_4F)(PEt_3)_2$ molecule with hydrogen atoms omitted for clarity. The vibrational ellipsoids are drawn at the 50% probability level.

Table V compares selected structural features of I, II, and III. The long Pt–Cl bond distance in I relative to II and III indicates a strong trans influence by the aryldiazo ligand. The value reported here of 2.413 (6) Å can be compared with a value of 2.422 (9) Å in $PtHCl(P(C_6H_5)_2C_2H_5)_2$ where the chlorine atom is trans to the highly trans labilizing hydride

Table V. Comparison of Structural Parameters of Compounds I, II, and III.

	 I	 II	 III
Pt-P, Å	2.302 (4)	2.320 (6)	2.328 (2)
Pt-Cl, Å	2.413 (6)	2.291 (2)	2.303 (2)
Pt-N(1), Å	1.975 (28)	1.973 (7)	2.081 (7)
N(1)-N(2), Å	1.17 (3)	1.235 (10)	1.436 (11)
N(2)-C(1), Å	1.49 (3)	1.412 (12)	1.408 (11)
Pt-N(1)-N(2), deg	118.3 (20)	125.3 (6)	113.2 (5)
N(1)-N(2)-C(1), deg	117.8 (23)	120.0 (8)	114.4 (7)

ligand.[12] The Pt–Cl bond length in II of 2.291 (2) Å can be taken as an indication that the aryldiazene ligand has little trans influence.[1] Protonation therefore may tend to decrease the metal-to-ligand bonding in the aryldiazo group. The aryldiazo ligand then might be expected to form a shorter Pt–N bond than either the diazene or hydrazine moieties.

The N(1)–N(2) bond shows a smooth increase in length from I to II to III but in view of the errors the difference between I and II is not significant. The N(1)–N(2) bond length in I of 1.17 (3) Å is intermediate between a double and a triple bond. Compounds II and III have N–N bond lengths corresponding respectively to double and single bonds. The Pt–N(1)–N(2) and N(1)–N(2)–C(1) angles are also consistent with this reduction of the N–N bond order. The N–N bond length found here is identical with that in a previously reported structure containing a doubly bent aryldiazo group.[8]

Compounds I, II, and III differ basically in the degree of N–N bond reduction. This is clearly indicated by the trends in N–N bond lengths and bond angles about each of the nitrogen atoms.

Although complexes of the type $Pt(NO)X(PR_3)_2$, X = halide or pseudohalide, have not yet been isolated, on the basis of their very close electronic resemblance to the present complex we anticipate that they will have square-planar coordination about the Pt atom and that the Pt–N–O angle will be bent. This geometry is to be contrasted with the pseudotetrahedral arrangement in $Ni(NO)(N_3)(PPh_3)_2$.[13]

Acknowledgment. We wish to thank the U. S. National Institutes of Health for their support of this work and Matthey-Bishop, Inc. for the generous loan of platinum used in this study.

Registry No. I, 55722-66-2.

Supplementary Material Available. Table II, the idealized hydrogen atom parameters, Table III, the root-mean-square amplitudes of vibration, and Table IV, a listing of structure amplitudes, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24X reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number AIC50289N-9-75.

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(5) In addition to various local programs for the CDC 6400 computer, modified versions of the following programs were employed: Zalkin's FORDAP Fourier summation program, Busing and Levy's ORFFE error function program, and Johnson's ORTEP thermal ellipsoid plotting program. Our full-matrix least-squares program NUCLS, in its nongroup form, closely resembles the Busing–Levy ORFLS program. Our absorption program is AGNOST.
(6) Scattering factors are from D. T. Cromer and J. T. Waber in "International Tables for X-Ray Crystallography", Vol. 4, Kynoch Press, Birmingham, England, 1974.
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Contribution from the Laboratoire de
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Formation and Crystal Structure of μ-Dioxo-bis(oxodiethyldithiocarbamatomolybdenum(V))

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It is well known that the dithiocarbamato ligand confers apparently unique properties to transition metal complexes, probably because of its important electron transfers to the metal. This may account in part for the renewed interest in the study of oxomolybdenum dithiocarbamates.[1]

Newton and coworkers have recently shown that molybdenum(IV) oxodithiocarbamates oxidatively add to organic molecules containing activated multiple bonds.[2] We have previously reported the crystal structure of the tetracyanoethylene complex[3] which is, as expected, heptacoordinate. In the course of these studies, we noticed that all solutions were readily decomposing, leading to purplish oils. We wish to report an analogous investigation on the behavior of the $MoO(Et_2NCS_2)_2$ addition to dimethyl acetylenedicarboxylate.

Experimental Section

All manipulations were carried out under argon, using solvents dried and stored under the same gas. Dimethyl acetylenedicarboxylate (Fluka) was degassed under vacuum and flash distilled prior to use. The dimethyl acetylenedicarboxylate–oxomolybdenumbis(diethyldithiocarbamate) complex was prepared after the procedure described by Newton and coworkers.[2]

The initially clear yellow solutions invariably darkened within a few hours.[2] Storing in the dark or at −28° did not inhibit this reaction. In all cases, small, well formed crystals appeared after 1 or 2 days. These were identified from infrared spectra as a μ-dioxo-molybdenum complex[4] and their structure was investigated in order to confirm this result.

Crystals of μ-dioxo-bis(diethyldithiocarbamatomolybdenum(V)) are triclinic, space group $P\bar{1}$ with $a = 8.121$ (2) Å, $b = 9.260$ (1) Å, $c = 13.921$ (1) Å, $\alpha = 107.77$ (2)°, $\beta = 101.54$ (2)°, $\gamma = 94.55$ (3)°, $V = 965.65$ Å^3, $M = 552$. The calculated density (1.898 g/cm^3) for $Z = 2$ is in good agreement with the observed density of 1.905 g/cm^3.

A rhombic crystal fragment having edges of 125 × 125 × 100 microns was used to record the intensity data in the range $6° < 2\theta < 75°$, using Mo Kα radiation. Data collection and structure refinement were conducted as previously described[5] and absorption corrections were applied using the program DATAPP.[6] Refinement of the structure using anisotropic temperature factors for all nonhydrogen atoms and isotropic temperature factors for the 20 hydrogen atoms lead to a conventional R factor of 0.032.[7]

Results and Discussion

The geometry of the complex is shown in Figure 1 and interatomic distances are listed in Table I.