Acknowledgment. We wish to thank Mr. G. Fekete for his assistance in obtaining crystallographic data.

Registry No. $Pt^{II}(HDPG)_2$, 55660-52-1; $Pt^{IV}(HDPG)_2Br_2$, 55660-53-2; $Pt^{IV}(HDPG)_2Cl_2$, 55660-54-3; $Pt^{IV}(HDPG)_2I_2$, 55660-55-4; $Pt^{IV}(HDPG)_2(SCN)_2$, 55660-56-5; $Pt(SEt_2)_2Cl_2$, 14873-92-8.

Supplementary Material Available. Tables III and IV giving the indexed powder pattern data for $M(HDPG)_2$ (M = Ni, Pd, Pt) and the electronic absorption spectra of bis(diphenylglyoximato) complexes, respectively, 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, 24× 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 $4.00 for photocopy or $2.50 for microfiche, referring to code number AIC50159E-9-75.

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Mixed-Ligand Five-Coordinate Complexes of Iridium(I)

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Ligand substitution and addition reactions with $IrCOCl(PPh_3)_2$ have been widely studied and show a marked dependence on the identity of the attacking reagent. Carbon monoxide adds to form $Ir(CO)_2Cl(PPh_3)_2$,[1] while $PMePh_2$ gives the unsaturated substitution product $IrCOCl(PMePh_2)_2$;[2] excess $PMePh_2$ has no effect.[3] $IrCOCl(PMePh_2)_2$, in turn, reacts with tertiary phosphites, L', in the presence of $NaBPh_4$ to give $[IrCO(PMePh_2)_2L'_2]BPh_4$.[3] $IrCOCl(PMe_2Ph)_2$ reacts with equimolar PMe_2Ph to produce $IrCOCl(PMe_2Ph)_3$, which has an extremely long iridium–chlorine bond in the solid state.[4] Two moles of PMe_2Ph produce $IrCO(PMe_2Ph)_4^+$, excess CO yields $Ir(CO)_3(PMe_2Ph)_2^+$, and equimolar PMe_2Ph and CO yield $Ir(CO)_2(PMe_2Ph)_3^+$.[5] $IrCOCl(PPh_3)_2$ reacts with $HPPh_2$ to give $IrCO(PHPh_2)_4^+$,[6] but PPh_3 gives $IrCO(PPh_3)_3^+$ salts only after preliminary removal of halide with Ag^+.[7]

Table I. ^{31}P NMR Parameters[a]

	δ(phosphite)	δ(phosphine)	J_{PP}
$P(OCH_2)_3CCH_3$	91.5[b]		
$Ir[P(OCH_2)_3CCH_3]_5^+$	84.70		
$Ir[P(OCH_2)_3CCH_3]_4(PPh_3)^+$	83.65	+1.99	54.0
$Ir[P(OCH_2)_3CCH_3]_3(PPh_3)CO^+$	80.42	−1.43	92.0
$Ir[P(OCH_2)_3CCH_3]_4CO^+$	80.50		
$Ir[P(OCH_2)_3CCH_3]_3(PPh_3)_2^+$	79.22	−1.15	49.5
$Ir[P(OCH_2)_3CCH_3]_2(PPh_3)_2CO^+$	78.36	+.58	44.0
$IrCOCl(PPh_3)_2$		+23.5	
PPh_3		−5.4	

[a] In $CHCl_3$ at 30°. [b] M. Crutchfield, C. Dungan, J. Letcher, V. Mark, and J. Van Wazer, *Top. Phosphorus Chem.*, **5**, 267 (1967).

Although caged phosphite esters[8] such as $P(OCH_2)_3CR$ seem suited to forming highly substituted phosphite complexes, the reactions of these ligands with second and third row transition metals have been little studied. We report here the results of a study of the reactions of $IrCOCl(PPh_3)_2$ and $IrN_2Cl(PPh_3)_2$ with $P(OCH_2)_3CCH_3$. The interpretation[3] of "virtually coupled" proton NMR spectra of $Ir(CO)_x(PR_3)_{5-x}^+$ complexes is not possible without knowledge of phosphorus–phosphorus coupling constants in a trigonal bipyramid. Values of $^2J_{PP}$ are reported here and are found to lie in narrow ranges which appear to be structurally diagnostic. Stereochemical nonrigidity is established for a number of products.

Experimental Section

$IrCOCl(PPh_3)_2$,[9] $IrN_2Cl(PPh_3)_2$,[10] and $P(OCH_2)_3CCH_3$[8] were prepared according to literature methods. Fourier transform ^{31}P NMR spectra were recorded with white-noise proton decoupling as described earlier.[11] Downfield chemical shifts are recorded as positive. Reactions were run and samples prepared under N_2.

$IrP(OCH_2)_3CCH_3]_5Cl \cdot p$-Xylene. One millimole of $Ir(CO)Cl(PPh_3)_2$ and 5 mmol of $P(OCH_2)_3CCH_3$ were stirred and refluxed in *p*-xylene for 2 hr. The resulting slurry was cooled and filtered, and the precipitate was vacuum dried. The infrared spectrum showed no CO stretching vibration, and no vibrations characteristic of PPh_3. Proton NMR (in $CDCl_3$): δ 4.16 (CH_2), 0.77 (CH_3); peaks due to *p*-xylene are also present in the correct intensity ratios at δ 6.98 (CH) and 2.25 (CH_3). Anal. Calcd for $C_{33}H_{55}ClIrO_{15}P_5$: C, 36.88; H, 5.12. Found: C, 36.56; H, 5.15.

Other reactions were run by adding 10 ml of benzene to a degassed sample of 0.1 g of the iridium compound and the appropriate amount of $P(OCH_2)_3CCH_3$. Gas evolution was vigorous, even for an iridium:phosphite ratio of 1:2. White solid formed immediately, but the reaction was stirred for 2 hr at 25° before filtration and vacuum drying.

Results

IrN_2ClL_2 reacts with L' (mole ratio 1:4.5) in benzene at 25° to precipitate a white solid which shows vibrational frequencies characteristic of both L and L';[12] no bands due to coordinated N_2 are present. Phosphorus NMR shows the product to be a mixture of IrL'_5^+ and IrL'_4L^+ in a mole ratio 1:5. The former was identified by independent synthesis (see below). The formula of the latter is based on the appearance of an A_4X spectral pattern with J_{AX} = 54.0 Hz.

When the reaction of IrN_2ClL_2 with L' is carried out at a 1:4 mole ratio, dinitrogen is still completely displaced. The benzene-insoluble material contains a trace of IrL'_5^+, along with equal amounts of IrL'_4L^+ and $IrL'_3L_2^+$. The latter shows an A_3X_2 spectral pattern with J_{AX} = 49.5 Hz.

$IrCOClL_2$ reacts with L' (mole ratio 1:5) in refluxing *p*-xylene with precipitation of analytically pure $[IrL'_5]Cl \cdot C_8H_{10}$. The chemical shift of this cation is shown in Table I.

Reaction of $IrCOClL_2$ with less than 5 mol of the caged phosphite at 25° produces numerous mixed-ligand cations. Using a 1:4 mole ratio in benzene at 25°, the following species were identified by phosphorus NMR. A small amount of $IrL'_5{}^+$ is evident from the singlet at 84.7 ppm. Moving upfield, the next spectral pattern is a doublet in the phosphite region with a separation (54 Hz) reproduced in a quintet in the phosphine region. This A_4X pattern is uniquely assignable to IrL'_4L^+. The spectral parameters of this ion are identical with the product from IrN_2ClL_2. Still further upfield is the most abundant species, a phosphite doublet which matches a phosphine quartet ($J = 92$ Hz). This A_3X pattern is attributed to $IrL'_3L(CO)^+$. This assignment is preferred over undissociated IrL'_3LCl on the basis of its insolubility in benzene; moreover, Cl^- is presumed to be more easily displaced than CO. Square planar IrL'_3L^+ would show a more complex AB_2X NMR pattern. A singlet, with a chemical shift nearly identical with that of $IrL'_3L(CO)^+$, is assigned to $IrL'_4(CO)^+$. Finally, a species showing phosphite and phosphine triplets ($J = 44$ Hz), an A_2X_2 pattern, is evident. This is assigned to $IrL'_2L_2(CO)^+$. The relative amounts of these species are as follows: $IrL'_5{}^+$, 1; IrL'_4L^+, 3.5; $IrL'_3L(CO)^+$, 10; $IrL'_4(CO)^+$, 1; $IrL'_2L_2(CO)^+$, 2.

If the benzene-insoluble solid described above is slurried for 2 hr in refluxing xylene, ligand redistribution occurs and only $[IrL'_5]Cl$ is present in the precipitate.

If the reaction of $IrCOClL_2$ with L' is performed with mole ratios of 1:3 and 1:2 in benzene at 25°, $IrL'_3L(CO)^+$ remains the major product, and the expected decreases are seen in the yields of $IrL'_5{}^+$, IrL'_4L^+, and $IrL'_4(CO)^+$. The mixture of products shows only a single carbonyl stretching frequency both in KBr (1973 cm^{-1}) and in $CHCl_3$ (2003 cm^{-1}). The benzene-insoluble fraction shows no evidence of $IrCOClL_2$, L', or L, in any of the reactions. Analysis of the benzene-soluble fraction shows only trace amounts of $IrCOClL_2$ (24.0 ppm in C_6H_6) and *no* L'. The main reactions of the caged phosphite are thus addition and displacement of chloride, to produce predominately ionic products.

Discussion

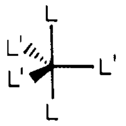
The reactions studied here produce labile mixtures of products. Thermodynamically, the most stable product appears to be $Ir[P(OCH_2)_3CCH_3]_5{}^+$,[13] even under conditions deficient in phosphite. This is presumably due to the small size of the phosphite and the strength of the iridium–phosphite bond. Even in the mixed ligand complexes, the data are most consistent with the production of coordinatively saturated species. High electron density at the metal has been stated to favor coordination number five for d^8 complexes.[14] Although it appears that the results with IrN_2ClL_2 and $IrCOClL_2$ suggest that chloride is readily displaced, our choice of a nonpolar solvent in effect encourages salt formation by removing them from solution. This solvent also performs a crude separation of salts from neutral species which facilitates product identification. Phosphorus NMR is especially suited to identifying the phosphorus–ligand stoichiometry of the products since there is an unequivocal separation in the chemical shifts of coordinated $P(OCH_2)_3CCH_3$ (75–85 ppm) and coordinated PPh_3 (+2 to −2 ppm). Note that the phosphite moves upfield on coordination while the phosphine moves downfield, both relative to the respective free ligand.

$IrL'_5{}^+$ is trigonal bipyramidal with an axial–equatorial $^2J_{PP}$ of 59 Hz. The cation undergoes intramolecular rearrangement in a manner consistent with the Berry process.[15]

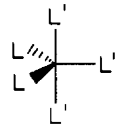
IrL'_4L^+ is presumably trigonal bipyramidal with PPh_3 positioned axially (C_{3v}) or equatorially (C_{2v}). In either case, the molecule must be nonrigid. If this cation is the C_{3v} isomer, the observed J includes a contribution from a large trans coupling constant. If it is the C_{2v} isomer, no such large component is averaged in. From the similarity of the value in IrL'_4L^+ (54 Hz) to that observed (Table I) in $IrL'_2L_2(CO)^+$ (44 Hz) and $IrL'_3L_2{}^+$ (49.5 Hz), we favor the isomer with triphenylphosphine equatorial.

The ^{31}P NMR singlet at 80.5 ppm is tentatively assigned to the ion $IrL'_4(CO)^+$, in which case this, too, must be a nonrigid molecule. This cannot be square planar $IrL'_4{}^+$ since the 80.5 ppm resonance is absent in the products of the reaction of L' with IrN_2ClL_2.

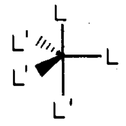
$IrL'_3L_2{}^+$ is produced only from IrN_2ClL_2, and not from $IrCOClL_2$. This implies that $P(OCH_2)_3CCH_3$ replaces N_2 in preference to PPh_3, but PPh_3 in preference to CO. Since two PPh_3 ligands are normally positioned trans in a trigonal bipyramid, structure I is favored. This is the structure of $Ir(CO)_3(PMe_2Ph)_2{}^+$.[16] Nonrigid structures such as II and III, while less likely, are nevertheless possible. At 30°, the lines due to IrL'_4L^+ are visibly broader than those of $IrL'_3L_2{}^+$. This supports the idea that $IrL'_3L_2{}^+$ is a rigid species (I), while IrL'_4L^+ is, of course, nonrigid.



I

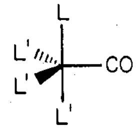


II

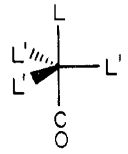


III

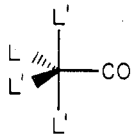
The $^2J_{PP}$ value observed for $IrL'_3L(CO)^+$ is almost twice as large as found in the other compounds studied here. Of the three possible isomers (IV–VI) for a compound of formula $IrL'_3L(CO)^+$, only one has L trans to one L'. A nonrigid molecule with structure IV is thus in best agreement with the data. If one assumes a value in the range 45–55 for a 90° L/L' coupling constant, the average J value of 92 in $IrL'_3L(CO)^+$ requires that the apical–apical coupling constant be 166–186 Hz.



IV

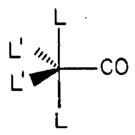


V



VI

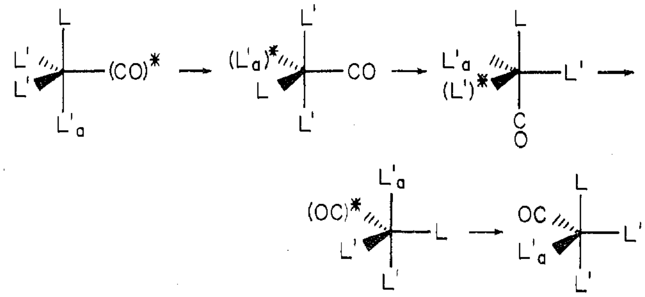
$IrL'_2L_2(CO)^+$ appears to have L' cis to L judging by the magnitude of $^2J_{PP}$. A structure (VII) with both PPh_3 ligands apical minimizes steric interactions[17] while simultaneously accommodating the π acceptor capacity of CO and $P(OCH_2)_3CCH_3$.[18]



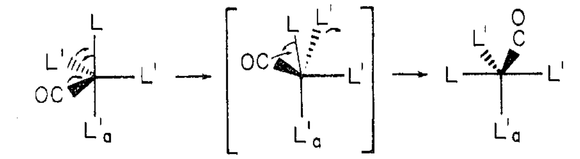
VII

Stereochemical nonrigidity is common for coordination number five. Of the molecules studied here, those with potentially equivalent phosphite ligands occupying inequivalent sites are invariably nonrigid. This applies to IrL'_5, IrL'_4L^+, $IrL'_3L(CO)^+$, and $IrL'_4(CO)^+$. The Berry process effects the interchanges observed for the D_{3h} and C_{3v} species $IrL'_5{}^+$, IrL'_4L^+ and $IrL'_4(CO)^+$. However, structure IV for $IrL'_3L(CO)^+$ has only a mirror plane, while a Berry process presumes at least C_{2v} symmetry. A single Berry process therefore does not equilibrate axial and equatorial phosphites.

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.

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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