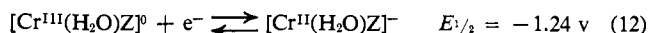
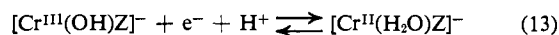


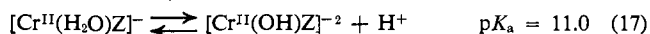
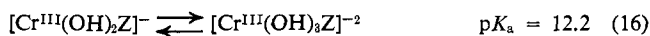
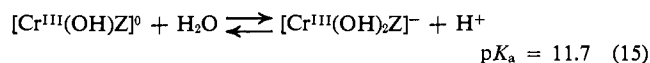
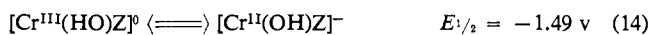
of 6.5, which is in good agreement with the pH value of the intersection of linear portions of a $E_{1/2}$ vs. pH plot. In the pH region 4–6, a simple reduction



takes place. Above pH 7, the reaction is the reduction of the deprotonated species with protonation



The extinction coefficient of the first band of the Cr(III) complex of H_3Z decreases markedly over the pH range 11.5–12.5. The extinction coefficient of the second band decreases over the pH range 10.5–12, but remains constant from 12 to 12.5. Above pH 10, the height of the reduction wave decreases with increasing pH, and the limiting current is diffusion controlled like that of the H_3QCOOH complex and not kinetically controlled like the complexes of H_3TOH or H_3XOH . The half-wave potential remains constant above pH 11.5. The following scheme provides a consistent explanation for these observations



The rate of the reverse reaction 15 is slow with respect to diffusion, and therefore the limiting current is diffusion controlled throughout, and $E_{1/2}$ can be evaluated. The existence of reaction 16 makes it difficult to compare polarographic and spectrophotometric values for the pK of reaction 15, but both sets of data are consistent with

the value of 11.8. A species analogous to the product of reaction 16 has been reported in the Fe(III)–EDTA system.¹¹

The acid–base changes near pH 12 for the H_3Z and H_3QCOOH complexes cannot be associated with dissociation of a ligand proton, since all of these are lost in acid solution for these two complexes. Addition of an OH^- , either by increase of coordination number of Cr(III) or by opening a chelate ring with or without rupture of a Cr–O bond, must be invoked.

The complexes of the ligands, H_3TOH and H_3XOH , which have an –OH functional group, lose a proton with K_a two orders of magnitude larger than those of ligands without a fourth replaceable proton. The rates of the associated protonations are of the order of magnitude ($\sim 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$) accessible to polarographic measurement. The rate constants for dissociation referred from these are less than 10^2 sec^{-1} .

These considerations leads us to postulate that, for the H_3TOH and H_3XOH complexes, the proton lost near pH 10 is that of the OH group. It is possible but not necessary that these reactions involve closure of an additional chelate ring. The observation that the rates of protonation associated with these changes are too slow to measure polarographically is consistent with this interpretation, as are the spectra.

Acknowledgment. We are grateful to Dr. Martin Rubin, Dr. Joseph Princiotto, and Mr. Edward Zapolski of the Georgetown University Medical Center and Dr. D. S. Lehman of the Dow Chemical Company, who generously supplied the ligands used in this study.

(11) R. Skockdople and S. Chaberek, *J. Inorg. Nucl. Chem.*, **11**, 222 (1960).

An Inorganic Analog of Nitrogen Reductase

George W. Parshall

Contribution No. 1269 from the Central Research Department, E. I. du Pont de Nemours and Company, Experimental Station, Wilmington, Delaware 19898. Received December 2, 1966

Abstract: The platinum hydride $(\text{Et}_3\text{P})_2\text{PtHCl}$ reacts with a diazonium salt in much the same way that a reducing enzyme is thought to react with a metal complex of N_2 in a biological system. The initial adduct, $[\text{ArN}=\text{NHPtCl}(\text{PEt}_3)_2]^+$, is reduced by $\text{Na}_2\text{S}_2\text{O}_4$ or H_2 to give $[\text{ArNHNH}_2\text{PtCl}(\text{PEt}_3)_2]^+$, ArN_2H_4^+ + $(\text{Et}_3\text{P})_2\text{PtHCl}$, and ArNH_2 + NH_4^+ in successive steps. The close analogy between this reduction and that occurring in nitrogen-fixing bacteria is consistent with the presence of a metal hydride in the biological system. A spectroscopic comparison of the two known classes of arylazometal complexes, $\text{ArN}=\text{NPtCl}(\text{PEt}_3)_2$ and $\text{ArN}=\text{NMo}(\text{CO})_2\text{C}_3\text{H}_5$, suggests a higher $\text{N}=\text{N}$ bond order in the molybdenum complexes.

Recent studies of biological nitrogen fixation have provided strong evidence for the involvement of transition metal ions. A protein fraction in cell-free extracts of *Azotobacter vinelandii* has the ability to reduce molecular nitrogen to ammonia.^{1,2} This enzyme system, which contains both molybdenum and iron,

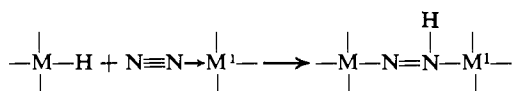
(1) W. A. Bulen, R. C. Burns, and J. R. Lecomte, *Proc. Natl. Acad. Sci. U. S.*, **53**, 532 (1965).

(2) R. W. F. Hardy and E. Knight, Jr., *Biochim. Biophys. Acta*, **122**, 520 (1966).

has at least two forms of activity. When supplied with adenosine triphosphate (ATP) and reducing potential (as $\text{Na}_2\text{S}_2\text{O}_4$ or reduced ferredoxin), the enzyme solutions evolve hydrogen. If N_2 is added to the solution, hydrogen evolution slows and ammonia forms. Metal ion involvement in these distinct hydrogenase and nitrogenase functions has been shown by inhibition experiments. Strong-field monodentate ligands, such as CO, inhibit nitrogen reduction but not hydrogen evolution.

Strong chelating ligands, for example, bipyridine, stop both reactions.

One hypothesis³ to account for the separate involvement of two metal ions is that one metal is present as a hydride and that the other forms at least a transient complex with N₂. The metal hydride may react with the nitrogen complex to give an adduct which is subsequently reduced stepwise to ammonia.



We now report a chemical system that reproduces several steps in this hypothetical reduction scheme. The significance of the comparison depends on two major assumptions: (1) a phosphine-stabilized platinum hydride may react like an ionic, amine-stabilized hydride of molybdenum or iron; (2) a benzenediazonium salt may be a reasonable model for a metal complex of N₂. The first assumption receives some support from recent work by Osborn, Powell, and Wilkinson.⁴ The hydride [(NH₃)₅RhH]²⁺ shows spectroscopic properties and chemical reactivity similar to those of (Et₃P)₂PtHCl⁵ used in the present work. It seems likely that the analogy will extend to amine-stabilized hydrides of other second-row transition metals.

The postulate that transition metal complexes of N₂ may behave as inorganic diazonium salts is more tenuous but is not inconsistent with available information. A preliminary crystal-structure determination on [(NH₃)₅RuN₂]₂ indicates that the coordinated nitrogen molecule in this complex is bound "end-on," analogous to a metal carbonyl.⁶ A comparison of the infrared spectra of known nitrogen complexes and their CO analogs (Table I) suggests that this may be a general phenomenon. The two principal resonance structures

Table I. N≡N and C≡O Stretching Frequencies

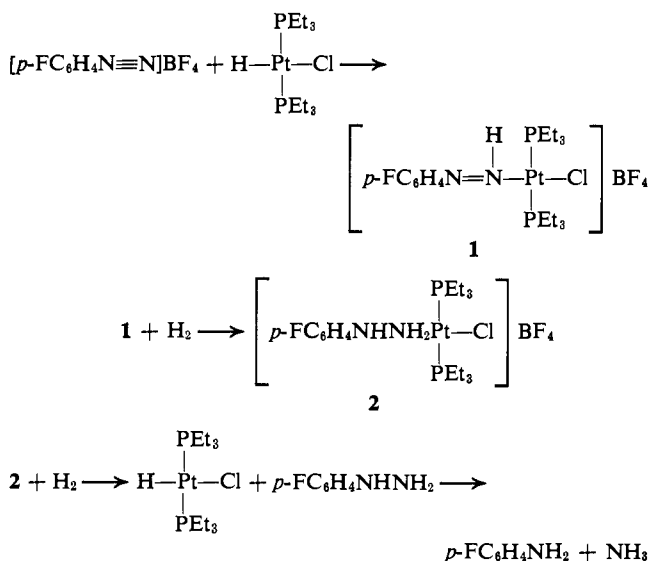
Compound	Ligand (L)	
	N≡N	C≡O
L	2331 ^a	2143 ^a
(Ph ₃ P) ₂ LIrCl	2095 ^b	1956 ^c
[(NH ₃) ₅ RuL](BF ₄) ₂	2154 ^d	...
Ni · L (chemisorbed)	2202 ^e	2040 ^f
B ₁₀ H ₈ (L) ₂	2250 ^g	2040 ^h
[C ₆ H ₅ L]BF ₄	2290	2212 ⁱ

^a Gas: K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, New York, N. Y., 1963, p 72. ^b J. P. Collman and J. W. Kang, *J. Am. Chem. Soc.*, **88**, 3459 (1966). ^c L. Vaska, *Science*, **152**, 769 (1966). ^d A. D. Allen and C. V. Senoff, *Chem. Commun.*, 621 (1965). ^e T. Nakata and S. Matsushita, *J. Catalysis*, **4**, 631 (1965). ^f R. P. Eischens, S. A. Francis, and W. A. Pliskin, *J. Phys. Chem.*, **60**, 194 (1956). ^g W. H. Knoth, *J. Am. Chem. Soc.*, **88**, 935 (1966). ^h W. H. Knoth, J. C. Sauer, H. C. Miller, and E. L. Muetterties, *ibid.*, **86**, 115 (1964). ⁱ PF₆ salt, G. A. Olah, S. J. Kuhn, W. S. Tolgyesi, and E. B. Baker, *ibid.*, **84**, 2733 (1962).

that stabilize a linear coordinated N₂ are expected to be M—N≡N and M=N+=N⁻. The former structure type apparently predominates in the classical benzenediazonium salts, but the latter structure may make a significant contribution for N₂ complexes of the late transition metals which possess large, filled d orbitals. The trend of N=N stretching frequencies suggests there is a continuum of bond types rather than an abrupt transition from one type to another.

Results

p-Fluorobenzenediazonium tetrafluoroborate reacts with (Et₃P)₂PtHCl rapidly and almost quantitatively to give the yellow crystalline *p*-fluorophenyldiimide complex **1**. The hydrogen on the nitrogen atom of this compound is acidic with a pK_a in ethanol of about 4.5. Removal of this proton with aqueous base gives a neutral, violet *p*-fluorophenylazoplatinum complex **3** described previously.⁷ The location of the proton was determined by terminal N¹⁵ substitution of the diazonium salt to give **1** with the N¹⁵ adjacent to the platinum atom. The proton nmr spectrum of N¹⁵-labeled **1** shows a sharp doublet (*J*_{NH} = 77 cps) at τ -5.1 consistent with the presence of the hydrogen on N¹⁵ rather than N¹⁴. The mild conditions of the reaction seem to preclude "scrambling" of the nitrogen atoms.⁸ The observed Pt¹⁹⁵-H coupling constant (80 cps) also supports the assigned structure.



The initial adduct (**1**) reacts rapidly with hydrogen (25°, 1 atm, Pt catalyst) to form the white *p*-fluorophenylhydrazine complex (**2**) in high yield. The same product is also formed by reduction with aqueous Na₂S₂O₄, but this reagent gives many by-products. Prolonged hydrogenation of **1** or **2** regenerates the original platinum hydride and gives *p*-fluorophenylhydrazine as its tetrafluoroborate salt. The latter, in turn, is slowly reduced to *p*-fluoroaniline and ammonia.

The N=N bond-saturation step is complete in about 1 hr, but the subsequent steps of Pt—N and N—N bond cleavage require a day or more for completion. This reaction rate differential permits easy isolation of the arylhydrazine complex (**2**). The low yield of **2** in the dithionate reduction is probably due to competitive nucleophilic reactions. The nitrogen ligands in **1** and **2** are quite vulnerable to nucleophilic attack. The aryl-diimide complex (**1**) reacts with tetraethylammonium

(7) G. W. Parshall, *J. Am. Chem. Soc.*, **87**, 2133 (1965).

(8) A. K. Bose and I. Kugajevsky, *ibid.*, **88**, 2325 (1966).

(3) R. W. F. Hardy and E. Knight, private communication.

(4) J. A. Osborn, A. R. Powell, and G. Wilkinson, *Chem. Commun.*, 461 (1966).

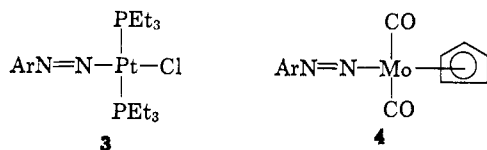
(5) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 5075 (1962).

(6) A. D. Allen and C. V. Senoff, *Proceedings of the Ninth International Conference on Coordination Chemistry*, St. Moritz, Switzerland, 1966, p 337.

chloride in acetone to give $[p\text{-FC}_6\text{H}_4\text{N}=\text{NHPtCl}(\text{PEt}_3)_2]\text{Cl}$, but the chloride salt is unstable. It decomposes rapidly in solution or more slowly in the solid state to give $(\text{Et}_3\text{P})_2\text{PtCl}_2$. The arylhydrazine complex (2) is attacked by chloride ion to give *p*-fluorophenylhydrazine and a mixture of *cis*- and *trans*- $(\text{Et}_3\text{P})_2\text{PtCl}_2$.

Polarographic reduction of the diimide complex (1) in acetonitrile shows a strong reductive wave at -0.92 vs. an $\text{Ag}|\text{AgNO}_3$ reference electrode, but the solution is not sufficiently stable for a thorough study of this process. The reduction potential corresponds roughly to -0.38 vs. the normal hydrogen electrode (ignoring junction potentials). Controlled current study of the reduction of the *p*-fluorophenylhydrazine complex (2) in CH_3CN gives reductive waves at -1.15 and -1.85 v.

Hydrogenation of the neutral arylazoplatinum compounds 3 ($\text{Ar} = \text{C}_6\text{H}_5$, *p*- FC_6H_4) under similar conditions gives the platinum hydride (58% yield) and a mixture of the arylhydrazine and aniline. The rate of hydrogen absorption is much slower than in the reduction of 1 and shows no sharp changes with time. If the reduction sequence is the same as that of the protonated species, the $\text{N}=\text{N}$ bond saturation step must proceed at a rate comparable to that of $\text{N}-\text{Pt}$ bond cleavage.



It was of interest to compare the spectral properties of the arylazoplatinum complexes (3) with the arylazomolybdenum compounds (4) of King and Bisnette.⁹ The phenyl and *m*- and *p*-fluorophenyl compounds of both series were prepared. The spectra are compared in Table II of the Discussion section. The $\text{N}=\text{N}$ vibration of 3 had not been assigned previously⁷ because it is in a region of the spectrum which contains strong C-H bending modes of the triethylphosphine ligand. In the *p*-fluorophenylazo complex, for example, $\nu_{\text{N}=\text{N}}$ appears at 1463 cm^{-1} as a shoulder on the strongest C-H band. However, isotopic substitution with ^{15}N adjacent to the platinum as in 1 produces the mathematically predicted shift to 1440 cm^{-1} . A similar ^{15}N -substitution experiment was done to verify the position of $\nu_{\text{N}=\text{N}}$ for the *p*-fluorophenylazomolybdenum compound.

Discussion

Nitrogen Reductase Analogy. The reductive sequence described above suggests that addition of a metal hydride to an N_2 complex is a reasonable process for nitrogen fixation. Some points of similarity between the synthetic model and the *Azotobacter vinelandii* enzyme system are worth noting.

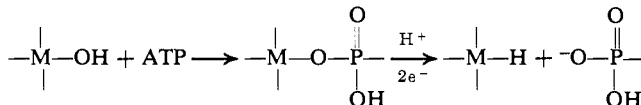
(1) The intermediates in both systems are stable to air and neutral water but are sensitive to acids and to nucleophiles such as chloride ion.

(2) The initial steps in reduction of the $\text{N}-\text{N}$ bond of complexed nitrogen are rapid. A high reaction rate, at least in the first step, is probably essential if the N_2 complex is unstable. The speed of these reductions

(9) R. B. King and M. B. Bisnette, *Inorg. Chem.*, **5**, 300 (1966).

may account for the failure to isolate intermediate reduction products such as $\text{HN}=\text{NH}$ from biological fixation systems.

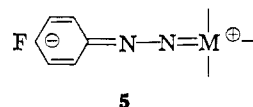
(3) The reduction potential of the synthetic system is approximately equal to that generated by the enzymatic reducing agent (about -0.4 v vs. the normal hydrogen electrode). The first two reductive steps in the synthetic model, formation of the metal hydride and saturation of the $\text{N}=\text{N}$ bond of the diimide complex, occur at the reducing potential of $\text{Na}_2\text{S}_2\text{O}_4$. The yield of $(\text{Et}_3\text{P})_2\text{PtHCl}$ from $(\text{Et}_3\text{P})_2\text{PtCl}_2$ is low but can probably be improved by replacement of chloride ion with a better "leaving group" such as tosylate or phosphate.¹⁰ One of the functions of adenosine triphosphate (ATP) in the biological system could be to provide a good "leaving group" for hydride formation



Comparison of Molybdenum and Platinum Azo Compounds. King and Bisnette⁹ proposed that the arylazomolybdenum compounds (4) which they prepared differ substantially from the arylazoplatinum compounds (3). The spectral properties of these two series of compounds (Table II) suggest that there are significant differences in character between the two sets of $\text{M}-\text{N}$ and $\text{N}=\text{N}$ bonds.

The $\text{N}=\text{N}$ stretching vibrations of the two classes of azo complexes show a difference of about 100 cm^{-1} . The lower values for the platinum compounds suggest a reduction in $\text{N}-\text{N}$ bond order. If we assume a complementary relationship between nitrogen-nitrogen and nitrogen-metal bond strengths (as is sometimes done for $\text{C}\equiv\text{O}$ and $\text{M}-\text{C}$ bonds in metal carbonyls⁹), the azoplatinum bond should be stronger than the azomolybdenum bond. This result would be consistent with a greater degree of π -back-bonding from the d^8 platinum to the nitrogen than from the d^4 molybdenum.

The F^{19} nmr spectra of the fluorophenylazo compounds support a similar conclusion. The F^{19} nuclei in both the *m*- and *p*-fluorophenylazoplatinum compounds are considerably more shielded than in the molybdenum analogs. The resonance structures such as 5 which enhance shielding of aromatic ring substituents would strengthen the metal-nitrogen bond and weaken the nitrogen-nitrogen bond.



The metal-ligand bonds in the two classes of arylazometal compounds also differ in reactivity. Although both classes are stable to nucleophilic attack on the metal atom, the molybdenum complexes are destroyed by reagents such as H_2 or HCl which cleanly remove the phenylazo moiety from the platinum compounds.

Experimental Section

General. The platinum compounds described below are relatively stable to air and water. Preparations and recrystallizations

(10) NOTE ADDED IN PROOF. The reaction of *trans-p*- $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{-PtCl}(\text{PEt}_3)_2$ with hydrogen at 1 atm and 25° for 23 hr gives $(\text{Et}_3\text{P})_2\text{PtHCl}$ in 50% yield. In contrast, *trans*- $(\text{Et}_3\text{P})_2\text{PtCl}_2$ does not react under these conditions.

Table II. Comparative Spectra of 3 and 4

Spectral property	$\text{C}_6\text{H}_5\text{N}=\text{N}-\text{M}$		$m\text{-FC}_6\text{H}_4\text{N}=\text{N}-\text{M}$		$p\text{-FC}_6\text{H}_4\text{N}=\text{N}-\text{M}$	
	Mo	Pt	Mo	Pt	Mo	Pt
$\nu_{\text{N}=\text{N}}, \text{cm}^{-1}$	1545 ^a	1440	Infrared		1562	1463
			Ultraviolet			
$\lambda, \text{m}\mu$	215 ^{a,b}	256 ^b	1565	1455	213 ^b	254 ^c
(ϵ)	(25, 500)	(16, 000)	(23, 900)	(17, 100)
$\lambda, \text{m}\mu$	296	290 sh	296	...	294	290
(ϵ)	(43, 300)		(34, 700)	...	(33, 500)	(11, 100)
$\lambda, \text{m}\mu$	419	335 sh	420	...	420	340 sh
(ϵ)	(7690)		(7890)	...	(6980)	(4660)
$\lambda, \text{m}\mu$...	535	520 sh	535	520	524
(ϵ)	...	(107)	(645)	(103)	(526)	(96)
			F ¹⁹ Nmr			
$\delta(\text{C}_6\text{H}_5)_2^d$	-1.85	0	+0.69	+2.89
$\delta(\text{CCl}_3\text{F})^e$	-2.09	-0.66	+0.43	+2.27

^a Data from ref 9. ^b Cyclohexane solution. ^c Dioxane solution. ^d Chemical shift in ppm relative to $\text{C}_6\text{H}_5\text{F}$, internal standard. Solution in Freon F-11, shielding parameter relative to $\text{C}_6\text{H}_5\text{F}$ calculated from the shift with respect to the solvent.

were done without protecting the solutions from the atmosphere. The *p*-fluorophenyl compounds were chosen for their convenient solubility properties and their marginally greater thermal stability compared to other arylazoplatinum derivatives.

In the N¹⁵-labeling experiments, commercial KNO₂ (83% purity, 98 atom % N¹⁵) was converted to NaNO₂ by ion exchange. The NaNO₂ was purified by crystallization. Other reagents were used as received.

Proton nmr spectra were determined on a Varian A-60 spectrometer with tetramethylsilane as an internal reference. Fluorine nmr spectra were measured at 56.4 Mc/sec on a Varian HR-60 spectrometer using ca. 10% solutions containing fluorobenzene as an internal reference. Infrared spectra were measured on a Perkin-Elmer 21 or 621 spectrometer using KBr pellets in the 400–4000-cm⁻¹ region and Nujol mulls in the low-frequency region to 200 cm⁻¹.

Syntheses. *p*-Fluorophenyldiimide Complex. *trans*-Chloro-*p*-fluorophenyldiimidebis(triethylphosphine)platinum tetrafluoroborate was prepared as described previously.⁷ For preparation of a N¹⁵-labeled sample, a solution of 0.65 g of *p*-fluoroaniline in 3 ml of 48% fluoroboric acid was treated with a solution of 0.40 g of NaN¹⁵O₂ in 1 ml of water at 0°. The *p*-fluorobenzenediazonium-N¹⁵ tetrafluoroborate showed N≡N stretching absorption at 2238 cm⁻¹ (KBr pellet) in contrast to a value of 2274 cm⁻¹ for the unlabeled salt.

The diazonium salt (0.55 g) was suspended in 10 ml of ethanol and was treated with a solution of 1.17 g of *trans*-chlorohydridobis(triethylphosphine)platinum in 5 ml of ethanol at 0°. The yellow-orange solution was cooled to -78° to give yellow crystals of the *p*-fluorophenyldiimide complex, mp 108–110° with decomposition and gas evolution. The infrared spectrum was identical with that of the unlabeled compound except for the shift of one peak from 1122 to 1101 cm⁻¹. Although this peak is somewhat obscured by BF stretching absorption, it is probably assignable to N=N stretching.

The proton nmr spectrum of the unlabeled *p*-fluorophenyldiimide complex contains peaks at τ -5.1, +2.05, 2.75, 8.22, and 8.87 with relative intensities of 1:2:2:12:18. The spectrum of the N¹⁵-labeled compound was almost superimposable except for the form of the peak at τ -5.1. In contrast to the broad featureless peak from the unlabeled compound, it appeared as a sharp doublet (J = 77 cps) with satellites due to Pt¹⁹⁵H coupling (J = 80 cps).

Titration of the *p*-fluorophenyldiimide complex with ethanolic KOH gave a neutralization equivalent of 657 (calculated value 677) with half-neutralization at pH 5.2. The reciprocal titration of *trans*-chloro-*p*-fluorophenyldiimidebis(triethylphosphine)platinum with ethanolic HCl gave a neutralization equivalent of 560 (calculated value 590) with half-neutralization at pH 3.8.

***p*-Fluorophenylhydrazine Complex.** A solution of 4.7 g of *trans*-chlorohydridobis(triethylphosphine)platinum in 25 ml of ethanol was added to a stirred, chilled solution of 2.1 g of *p*-fluorobenzenediazonium tetrafluoroborate in 50 ml of ethanol. The mixture was warmed to room temperature over a period of 20 min. A 5% platinum-on-carbon catalyst (0.10 g) was added, and hydrogen was bubbled through the mixture for 1 hr. The mixture was filtered to remove a mixture of catalyst and white crystalline product. Cooling the filtrate gave 1.6 g of faintly yellow crystals. The total weight

of crude product was 5.9 g. Recrystallization of the combined products from ethanol gave fine white needles of *trans*-chloro-*p*-fluorophenylhydrazinebis(triethylphosphine)platinum tetrafluoroborate, mp 183–184° with decomposition to a red liquid, yield 3.4 g (50%).

Anal. Calcd for C₁₃H₃₇BClF₅N₂P₂Pt: C, 31.79; H, 5.49; N, 4.12; Pt, 28.7. Found: C, 31.65; H, 5.70; N, 4.29; Pt, 28.8.

The proton nmr spectrum was determined in acetone-*d*₆. There were peaks at τ 2.8, 3.2, 3.7, 7.98, and 8.79 with relative intensities of 4.8, 1.8, 0.7, 14.0, and 18.0. Addition of acetic acid-*d*₄ to the solution broadened the peaks at τ 3.2 and 3.7 until they were undetectable but the other peaks were not affected. Hence, these two peaks are probably assignable to NH protons.

***p*-Fluorophenyldiimide Complex.** Sodium cyclopentadienyltricarbonylmolybdate was prepared from excess sodium amalgam and 5.5 g of cyclopentadienyltricarbonylmolybdenum dimer in 100 ml of tetrahydrofuran. The solution was decanted from the sodium amalgam and was chilled to -78°. *p*-Fluorobenzenediazonium tetrafluoroborate (3.15 g) was added in portions, and the mixture was allowed to warm to room temperature over a period of 2 hr. The solvent was evaporated under reduced pressure, and the sticky red residue was extracted with two 50-ml portions of dichloromethane. The extract was evaporated to dryness and the residue was chromatographed on neutral alumina (activity grade 2) in ether. The red eluate was evaporated to dryness and the residue was recrystallized from hexane to give red crystals of cyclopentadienyl-*p*-fluorophenyldiimidecarbonylmolybdenum, mp 81–82°, yield 4.0 g.

Anal. Calcd for C₁₃H₉FMoN₂O₂: C, 45.90; H, 2.67; N, 8.24. Found: C, 46.17; H, 2.89; N, 8.63.

The infrared spectrum showed N=N stretching at 1562 cm⁻¹ and C≡O stretching at 1878, 1890, and 1980 cm⁻¹. In a sample prepared from the N¹⁵-labeled diazonium salt, the N=N absorption appeared at 1535 cm⁻¹.

***m*-Fluorophenyldiimide Complex.** The preparation was carried out as was described for the *p*-fluorophenylazo complex. Crystallization from hexane gave fine red needles of cyclopentadienyl-*m*-fluorophenyldiimidecarbonylmolybdenum, mp 67°, yield 3.9 g.

Anal. Calcd for C₁₃H₉FMoN₂O₂: C, 45.90; H, 2.67; N, 8.24. Found: C, 45.54; H, 3.25; N, 8.26.

The infrared spectrum contained N=N stretching at 1565 cm⁻¹ and C≡O stretching at 1894, 1912, and 1973 cm⁻¹.

Reductions. The comparative rates of reduction of the *p*-fluorophenyldiimide complex and of the neutral *p*-fluorophenylazo compound were studied in a microhydrogenation apparatus at 32°. Duplicate 10-mg samples were hydrogenated over platinum dioxide in ethanol at 1 atm hydrogen pressure. The *p*-fluorophenyldiimide complex underwent 60% hydrogenation (relative saturation of the N=N) in 1 hr and 90% saturation in 6 hr, whereas periods of 18 and 44 hr were required for corresponding hydrogenation of the neutral compound. Preparative experiments in which the products were isolated are described below.

Reduction of Diimide Complex to Hydrazine Complex. A mixture of 1.00 g of *trans*-chloro-*p*-fluorophenyldiimidebis(triethylphosphine)platinum tetrafluoroborate, 0.08 g of platinum dioxide,

and 25 ml of ethanol was stirred in a hydrogen atmosphere at 32° for 50 min. The mixture was evaporated to dryness, and the residue was recrystallized from methanol to give white crystals of the *p*-fluorophenylhydrazine complex described above, mp 184–188° dec.

A solution of 0.68 g of the *p*-fluorophenyldiimide complex in 15 ml of ethanol was stirred at 25° while a solution of 0.21 g of $\text{Na}_2\text{S}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in 2 ml of water was added. The yellow solution became red and an off-white solid separated. The mixture was stirred for 1 hr and was filtered and evaporated to give a sticky yellow residue. Extraction of the residue with ethanol gave a yellow solution from which the *p*-fluorophenylhydrazine complex precipitated on cooling, mp 176–179° dec. The infrared spectrum was identical with that of the material obtained by hydrogenation.

Exhaustive Hydrogenation of the Diimide Complex. A mixture of 1.0 g of *trans*-chloro-*p*-fluorophenyldiimidebis(triethylphosphine)platinum tetrafluoroborate and 0.10 g of 5% platinum on carbon in 25 ml of ethanol was hydrogenated at 70–75° and 4.5 atm for 10 hr. The reaction mixture was filtered and the filtrate was evaporated under reduced pressure to give a yellow gum. Extraction with hexane and with water dissolved most of the gum. Chilling the hexane extract gave 0.45 g (65%) of fine white needles of *trans*-chlorohydridobis(triethylphosphine)platinum, mp 79–80°. The infrared spectrum was identical with that of an authentic sample.

The aqueous extract was treated with aqueous picric acid solution to give a yellow precipitate. Recrystallization from water gave 0.13 g (25%) of fine yellow needles of *p*-fluorophenylhydrazinium picrate. The picrate melted at 140–143° with gas evolution. The X-ray powder pattern was identical with that of an authentic sample. In addition, a trace of *p*-fluoroanilinium picrate was isolated by mechanical sorting of the crystals. The orange-brown crystals melted with sublimation and decomposition at 163–175°.

Hydrogenation of the Neutral Azo Compound. A solution of 1.0 g of *trans*-chloro-*p*-fluorophenylazobis(triethylphosphine)platinum in 25 ml of ethanol was hydrogenated over 0.10 g of 5% platinum on carbon at 55° and 4.5 atm for 18 hr. Isolation of the products, as in the preceding experiment, gave 0.46 g (58%) of *trans*-chlorohydridobis(triethylphosphine)platinum, mp 80°, and a mixture of *p*-fluoroanilinium and *p*-fluorophenylhydrazinium picrates.

Hydrogenation of *p*-fluorophenylhydrazinium chloride under the same conditions gave, as a major product, *p*-fluoroaniline which was identified as its picrate salt and by its gas chromatographic retention time.

Dithionite Reduction of $(\text{Et}_3\text{P})_2\text{PtCl}_2$. A solution of 0.42 g of $\text{Na}_2\text{S}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in 5 ml of water was added dropwise to a boiling solution of 1.0 g of *cis*-dichlorobis(triethylphosphine)platinum in 25 ml of ethanol. The mixture became orange, but the color faded over a period of 30 min. The solution was cooled and was evaporated

to give a yellow syrup. The residue was extracted successively with hexane, ether, acetonitrile, and water. Chilling the hexane extract gave about 10 mg of *trans*-chlorohydridobis(triethylphosphine)platinum, mp 80°. The infrared spectrum was identical with that of an authentic sample. Approximately 50 mg of the hydride was obtained from the ether extract. The aqueous extract deposited off-white crystals which decomposed during attempted recrystallization from ethanol to give *trans*-dichlorobis(triethylphosphine)platinum, mp 137–140°.

Reaction of Cationic Complexes with Chloride Ion. *p*-Fluorophenyldiimine Complex. A solution of 0.22 g of tetraethylammonium chloride hydrate in 1 ml of ethanol was added to a solution of 0.68 g of *trans*-chloro-*p*-fluorophenyldiiminebis(triethylphosphine)platinum tetrafluoroborate in 4 ml of acetone. After about 30 sec, a yellow solid crystallized from the solution, yield 0.53 g, mp 112–113° dec.

Treatment of a portion of the yellow solid with sodium acetate in ethanol gave the violet color of *trans*-chloro-*p*-fluorophenylazobis(triethylphosphine)platinum. The analysis of the crude yellow solid corresponded to $[\text{p-FC}_6\text{H}_4\text{N}=\text{NHPtCl}(\text{PEt}_3)_2]^+\text{Cl}^-$, but the solid always decomposed during recrystallization attempts. The proton nmr spectrum in chloroform-*d* showed peaks at τ –4.0, +2.5, 8.05, and 8.83 with intensity ratios of 1:5:12:18.

Anal. Calcd for $\text{C}_{18}\text{H}_{34}\text{Cl}_2\text{FN}_2\text{P}_2\text{Pt}$: C, 34.50; H, 5.63; Cl, 11.3. Found: C, 34.58; H, 5.59; Cl, 11.1.

Attempted recrystallization of the yellow solid from methanol or ethanol gave a mixture of *cis*- and *trans*-dichlorobis(triethylphosphine)platinum, both of which were identified by their melting points and infrared spectra.

***p*-Fluorophenylhydrazine Complex.** A solution of 0.68 g of *trans*-chloro-*p*-fluorophenylhydrazinebis(triethylphosphine)platinum tetrafluoroborate and 0.16 g of lithium chloride in 15 ml of methanol was stirred at room temperature for 4 hr. The mixture was then evaporated to dryness. The residue was extracted successively with ether, water, and warm methanol. Evaporation of the ether extract gave 0.06 g of *trans*-dichlorobis(triethylphosphine)platinum, mp 138–140°. The methanol extract gave 0.43 g of the *cis* isomer as white crystals, mp 193–194°. The combined yield of dichloro compounds was 0.49 g (98%). Addition of picric acid solution to the aqueous extract gave a yellow precipitate of *p*-fluorophenylhydrazinium picrate. Recrystallization from water gave yellow needles with a melting point of 134–135° dec. The X-ray powder pattern was identical with that of an authentic sample.

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