Acknowledgments. Preliminary studies on this system were carried out by H. M. Stanford. Dr. R. R. Holmes of the Bell Telephone Laboratories gave many

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valuable suggestions for constructing the calorimeter system. We also profited from conversations with Professor R. P. Bell, F.R.S., and suggestions from Professor P. H. Rieger. This research was supported in part by the Advanced Research Projects Agency, Department of Defense.

Arylazoplatinum Compounds

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Several arylazoplatinum compounds, Ar-N=N-PtCl- $[P(C_2H_5)_3]_2$, have been prepared by the reaction of arenediazonium salts with $HPtCl[P(C_2H_5)_3]_2$. The azo compounds are stable, highly colored solids which may be decomposed catalytically to give the corresponding arylplatinum compounds, trans- $ArPtCl[P(C_2H_5)_3]_2$. Spectral studies of these complexes indicate substantial interaction of the platinum d-orbitals with the azo π orbitals.

The reaction of diazonium salts with metal halides has been used extensively for the preparation of arylmetal compounds.1 Arylazometal complexes were postulated as intermediates in this reaction but no such compounds were isolated until recently when King and Bisnette² described *p*-anisylazo- π -cyclopentadienyldicarbonylmolybdenum. It has been suggested that a Co-N bond exists in cobalt chloride complexes of benzenediazonium chlorides.³ However, more recent spectroscopic studies⁴ indicate that the spectral shifts ascribed to Co-N bonding were actually due to charge-transfer phenomena.

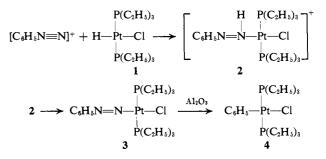
Arylazoplatinum compounds in which an arylazo function is σ -bonded to platinum have now been prepared.

Synthesis. Benzenediazonium tetrafluoroborate reacts with *trans*-chlorohydridobis(triethylphosphine)platinum⁵ (1) to give a yellow crystalline salt which probably has structure 2. Treatment of this salt with methanolic KOH gives red crystals of trans-chloro-(phenylazo)bis(triethylphosphine)platinum (3). Products corresponding to 3 have also been obtained by reaction of *m*-fluoro-, *p*-fluoro-, and *p*-nitrobenzenediazonium salts with the hydride (1). Reaction of p-methoxybenzenediazonium tetrafluoroborate with 1

(4) (a) E. A. Boudreaux, H. B. Jonassen, and L. J. Theriot, J. Am. Chem. Soc., 85, 2039, 2896 (1963); (b) R. H. Nuttall, E. R. Roberts, and D. W. A. Sharp, Spectrochim. Acta, 17, 947 (1961).

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

gave only the p-methoxyphenylplatinum compound analogous to 4.



The initial step in the reaction sequence is probably addition of the diazonium salt to the square-planar platinum complex followed by migration of a hydrogen from the platinum to the adjacent nitrogen atom to give 2. A similar proton transfer has been observed in the reaction of diazonium salts with the $B_{10}H_{10}^{-2}$ ion.⁶ The proton n.m.r. spectra of **2** and the analogous *m*- and *p*-fluorophenyl complex salts in $CDCl_3$ show peaks at ca. $\tau - 5^7$ assignable to the NH proton. The phenyl salt (2) gives a fairly sharp peak. On dilution with trifluoroacetic acid, proton exchange occurs, and the peak is broadened and shifted to higher field.

The neutral azo complexes (3) are red or green crystalline solids which melt to give highly colored liquids. The melts decompose with evolution of nitrogen at ca. 120°. Solutions in hydrocarbon solvents appear to be stable for several days. Solutions in CCl₄ or CHCl₃ rapidly decolorize with evolution of nitrogen.

Attempts to chromatograph the neutral compounds on active neutral alumina gave only trans-arylchlorobis-(triethylphosphine)platinum derivatives such as 4. Although several of these compounds have been prepared by Grignard reactions,⁸ the catalytic decomposition of the arylazo complexes is probably an equally convenient route to the *trans* series. This route is particularly valuable for synthesis of compounds such

⁽¹⁾ A. N. Nesmeyanov, "Selected Works in Organic Chemistry," translated by A. Birron and Z. S. Cole, The Macmillan Co., New York, N. Y., 1963, presents numerous examples of this technique

⁽²⁾ R. B. King and M. B. Bisnette, J. Am. Chem. Soc., 86, 5694 (1964).

⁽³⁾ L. A. Kazitsina, O. A. Reutov, and Z. F. Buchovskii, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1523 (1960).

⁽⁶⁾ M. F. Hawthorne and F. P. Olsen, J. Am. Chem. Soc., 86, 4219 (1964).

⁽⁷⁾ $\tau = 10 - \Delta(Me_4Si)/oscillator$ frequency: G. V. D. Tiers, J. Phys. Chem., 62, 115 (1958).

⁽⁸⁾ J. Chatt and B. L. Shaw, J. Chem. Soc., 4020 (1959).

as the *p*-nitrophenyl derivatives which are not accessible by the Grignard method. The *trans* configurations of the known phenyl compound **4** and the analogous fluorophenyl compounds were established by comparison with authentic samples.

The reaction of *p*-fluorobenzenediazonium tetrafluoroborate with the platinum hydride (1) gave a small but significant amount of *trans*-di-*p*-fluorophenylbis(triethylphosphine)platinum. This compound is presumably formed by a secondary reaction of *p*- $FC_6H_4PtCl[P(C_2H_5)_3]_2$ with the diazonium salt.

Spectral Characteristics

The *trans* configuration was assigned to the azoplatinum compounds by the proton n.m.r. technique of Jenkins and Shaw.⁹ The methyl resonance patterns of these complexes appear as five-line structures with line separations of 8 c.p.s. This pattern is almost certainly due to coupling of the CH₃ protons with the CH₂ protons of the ethyl group and with the two *trans*phosphorus atoms acting as a pair. ($J_{CH_3CH_3} = 8$ c.p.s., $J_{PH+P'H} = 16$ c.p.s.). Proton spin decoupling by irradiation of the sample with the CH₂ resonance frequency reduced the CH₃ resonance to a simple 1:2:1 triplet. This simple structure strongly indicates virtual coupling of the CH₃ protons with two *trans*phosphorus atoms.

Infrared spectra were recorded for the aryl- and arylazoplatinum complexes over the range 400–4000 cm.⁻¹. No bands assignable to N=N stretching were detected by comparison of the 1500–1600-cm.⁻¹ absorption bands of the two classes of compounds (Table I). The only significant difference in this range is that the aromatic C=C bands of the azo complexes fall at slightly higher frequencies than do those of the aryl-platinum complexes.

Table I. Infrared Spectra (cm. -1)

| Aryl group | ArPtCl- $[P(C_2H_5)_3]_2$ | $ArN = NPtCl- [P(C_2H_5)_3]_2$ | |
|--|------------------------------|--------------------------------|--|
| C ₆ H ₅ | 1561, 1574 | 1592, 1596 | |
| $p-NO_2C_6H_4$ | 1555, 1582 | 1596, 1614 | |
| p-FC _t H₄ | 1581 | 1596 | |
| m-FC ₆ H ₄ | 1560, 1587 | 1566, 1593 | |
| p-CH ₃ OC ₆ H ₄ | 1562, 1592 | | |

The electronic spectra (Table II) of all the azo complexes show weak bands in the visible region assignable to the N=N transitions. The *p*-nitrophenylazo derivative is green; the others are red. Both the aryland arylazo compounds show strong absorption throughout the ultraviolet range. The weakness of the azo band and the enhancement of the aromatic bands in the arylazo complexes suggest effective conjugation of the azo function with the π -system of the aromatic ring.

The F^{19} nuclear magnetic resonance spectra of the *m*- and *p*-fluorophenyl- and *m*- and *p*-fluorophenylazoplatinum compounds are shown in Table III. The spectra of the *m*- and *p*-fluoroazobenzenes are shown for comparison.

Table II. Electronic Spectra of Platinum Complexes

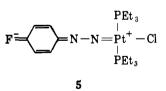
| | ArN=NPtCl(PEt ₃) ₂ | | ArPtCl(PEt ₃) ₂ | |
|--|---|--------|--|--------|
| Aryl group | λ, Å. | e | λ, Å. | e |
| C ₆ H ₅ | 5300 | 109 | | |
| | 3400 sh | 5720 | 2640 | 5500 |
| | 2900 | 10,900 | 2480 sh | 7450 |
| | 2550 | 15,400 | 2300 | 11,700 |
| <i>m</i> -FC ₆ H₄ | 5350 | 103 | | |
| | Strong end | | 2800 sh | 2780 |
| | absorption | | 2720 sh | 4120 |
| | - | | 2650 sh | 4570 |
| | | | 2500 sh | 6290 |
| | | | 2320 sh | 12,900 |
| <i>p</i> -FC ₆ H₄ | 5240 | 96 | | |
| | 3400 sh | 4660 | 2880 sh | 2140 |
| | 2900 sh | 11,100 | 2800 sh | 2660 |
| | 2540 | 17,100 | 2530 | 5140 |
| p-NO₂C ₆ H₄ | 6000 | 226 | | |
| | 3130 | 21,600 | 3350 | 13,500 |
| P-CH ₃ OC ₆ H ₄ | | | 2900 | 3040 |
| | | | 2360 | 15,000 |

Discussion

The infrared and ultraviolet spectra suggest conjugation of the aromatic, N=N, and Pt π -systems, but the evidence is tenuous. More substantial evidence is provided by the F¹⁹ n.m.r. spectra of the fluorophenyl derivatives.

Taft and his co-workers¹⁰ have shown that the F^{19} shielding parameter of a substituted fluorobenzene is a sensitive criterion of the electronic influence of the substituent. Application of this technique to fluorophenylbis(triethylphosphine)platinum compounds has shown extensive electron transfer from the platinum d-orbitals to the benzene π -orbitals.¹¹ This donor action produces positive shielding of the F¹⁹ nuclei in both the *meta* and *para* compounds (Table III).

An azo substituent on a benzene ring ordinarily withdraws electrons by a resonance mechanism as shown by the strongly negative F^{19} shielding parameter of *p*fluoroazobenzene (Table III). In contrast, the platinumazo substituent is a strong donor in *p*-FC₆H₄N= NPtCl(PEt₃)₂. This result suggests that resonance structures such as **5** make substantial contributions to the electronic character of the arylazoplatinum compounds.



One consequence of the existence of resonance structures such as 5 is a weakening of the N=N bond. Since this canonical form contributes significantly to the structure of the metal azo compounds, hydrogenolysis of the N-N bonds should be facilitated. Similarly, in the M-N=N-M structures proposed as intermediates in the biological fixation of nitrogen,¹² cleavage of the N=N bond might be expected. Unless one of the intermediate reduction products such as diimine or hydrazine were released from the complex by

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- (12) M. K. Bach, Biochem. Biophys. Acta, 26, 104 (1957).

⁽⁹⁾ J. M. Jenkins and B. L. Shaw, Proc. Chem. Soc., 279 (1963).

⁽¹⁰⁾ R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, J. Am. Chem. Soc., 85, 709, 3146 (1963).

Table III. F¹⁹ N.m.r. Shielding Parameters^{a,b} for Substituted Fluorobenzenes

| Compound | para isomer | | meta isomer | |
|--|--------------------|------------------|--------------------|----------------------|
| | CCl ₃ F | Cyclo- hexane | CCl ₃ F | Cyclo- hexane |
| FC ₆ H ₄ PtCl(PEt ₃) ₂ | +10.0 | +10.3 | +2.27 | +2.50 |
| $ FC_{6}H_{4}N = N - PtCl(PEt_{3})_{2} FC_{6}H_{4}N = NC_{6}H_{5} $ | +2.27 | +2.89 .17° | -0.66 -0 | <i>ca.</i> 0 .78° |

^a Shielding parameter $\int_{C_{6}H_{6}F} X_{C_{6}H_{4}F} = (H_{XC_{6}H_{4}F} - H_{C_{6}H_{6}F})/H_{C_{6}H_{6}F} \times 10^{6}$; ref. 10. ^b Spectra were determined at 56.4 Mc./sec. on 5-10% solutions with CCl₃F or fluorobenzene as an internal standard. ^c Average of CCl₄ and cyclohexane solution values. The value for the *para* compound is from ref. 10. The author is indebted to the referee for the *meta* parameter.

steric factors as suggested by Azim and Roberts,¹³ one would not expect to detect N—N species in biological systems.

Experimental

Phenylazoplatinum Complex. (a) A suspension of 1.44 g. of benzenediazonium tetrafluoroborate in 15 ml. of ethanol was stirred at 0° while a solution of 4.20 g. of *trans*-chlorohydridobis(triethylphosphine)platinum was added. The mixture gave a clear yellow-orange solution which soon deposited yellow needles of the tetrafluoroborate salt. The crystals were filtered, washed with ether, and dried under vacuum; yield 3.5 g. (75%), m.p. 109-110° dec.

Anal. Calcd. for $C_{18}H_{36}BClF_4N_2P_2Pt$: C, 32.76; H, 5.50. Found: C, 32.61; H, 5.41.

The proton n.m.r. spectrum (60 Mc./sec., CDCl₃ solution, Me₄Si internal reference) showed three types of protons in a 30:5:1 ratio. The high-field group (30) showed the same structures centered at τ 8.14 and 8.80 as the other *trans*-bis(triethylphosphine)platinum compounds. A group of relative intensity 5 with peaks at τ 2.11 and 2.25 is assignable to the phenyl protons. Finally, a triplet (intensity 1) centered at τ -5.2 is assignable to NH.

(b) A solution of 0.85 g. of the phenylazoplatinum tetrafluoroborate from part a in 5 ml. of methanol was stirred and chilled while a solution of 0.18 g. of sodium acetate trihydrate in 1 ml. of methanol was added. The mixture became red immediately and violet crystals began to separate. The mixture was promptly filtered, and the solid was recrystallized from hexane to give red-violet needles of *trans*-chlorophenylazobis(triethylphosphine)platinum, m.p. $109.5-110.5^{\circ}$.

Anal. Calcd. for $C_{18}H_{35}ClN_2P_2Pt$: C, 37.79; H, 6.33; N, 4.88. Found: C, 37.63; H, 6.21; N, 4.80.

(c) Chromatography of the product from part b on neutral alumina gave an initial red band which decolorized on elution with a benzene-hexane mixture. The chief crystalline product was *trans*-chlorophenylbis(triethylphosphine)platinum, m.p. $104-105^{\circ}$ (lit.⁸ m.p. $105-107^{\circ}$). The infrared spectrum was identical with that of an authentic sample,⁸ and a mixture melting point was not depressed.

Anal. Calcd. for $C_{18}H_{35}ClP_2Pt$: C, 39.75; H, 6.50. Found: C, 39.69; H, 6.43.

m-Fluorophenylazoplatinum Complex. (a) A suspension of 0.58 g. of *m*-fluorobenzenediazonium tetrafluoroborate in 15 ml. of ethanol was stirred at 0° while a solution of 1.40 g. of *trans*-chlorohydridobis-(triethylphosphine)platinum in 7 ml. of ethanol was

(13) M. A. Azim and E. R. Roberts, Biochem. Biophys. Acta, 21, 562 (1956).

added. All the diazonium salt dissolved to give a clear orange solution. Yellow crystals began to separate from the solution within 50 sec. The mixture was filtered under nitrogen pressure, and the crystals were washed with ethanol and ether. The crystals were dried at 25° (10^{-3} mm.) for 2 hr.; yield 0.97 g., m.p. $108-110^{\circ}$ dec.

Anal. Calcd. for $C_{18}H_{35}BClF_5N_2P_2Pt$: C, 31.89; H, 5.20; N, 4.13; F, 14.01. Found: C, 31.85; H, 5.33; N, 4.47; F, 14.59.

The F¹⁹ n.m.r. spectrum (dilute solution in acetone, some gas evolution during solution) showed a large peak at +8525 c.p.s. from CFCl₃ (external substitution, 56.4 Mc./sec.) assignable to BF₄⁻ and a small peak at +8480 c.p.s.

(b) A solution of 0.52 g. of the fluoroborate salt from part a in 4 ml. of methanol was treated with a solution of 0.10 g. of sodium acetate trihydrate in 1 ml. of methanol at 0°. No crystals separated although the mixture did become red-violet. When the solution was cooled to -78° , violet crystals appeared. The supernatant liquid was decanted, and the crystals were dried under vacuum. The dry, violet solid was recrystallized from hexane to give violet crystals of *trans*-chloro-*m*-fluorophenylazobis(triethylphosphine)platinum, m.p. 38°.

Anal. Calcd. for $C_{18}H_{34}ClFN_2P_2Pt$: C, 36.64; H, 5.81. Found: C, 36.80; H, 5.85.

Catalytic decomposition of the azo compound on alumina gave *trans*-chloro-*m*-fluorophenylbis(triethylphosphine)platinum as short off-white needles, m.p. 90-91°. A mixture melting point with an authentic sample was not depressed.

p-Fluorophenylazoplatinum Complex. (a) A solution of 2.30 g. of *trans*-chlorohydridobis(triethylphosphine)platinum in 12 ml. of ethanol was added to a chilled and stirred suspension of 1.05 g. of *p*-fluorobenzenediazonium tetrafluoroborate in 25 ml. of ethanol. The clear yellow-orange solution was stirred at 0° for 30 min. After 10 min., a yellow-orange solid crystallized. The crystals were filtered and were washed with ethanol and ether, yield 1.90 g., m.p. $105-106^{\circ}$.

Anal. Calcd. for $C_{18}H_{35}BClF_{5}N_{2}P_{2}Pt$: C, 31.89; H, 5.20. Found: C, 32.53; H, 5.51.

The F¹⁹ n.m.r. spectrum (56.4 Mc./sec.) of a 15% solution in CDCl₃ showed a sharp signal at +6135 c.p.s. and a strong broad signal, probably assignable to BF_4^- , at +8585 c.p.s. (CCl₃F internal standard). The proton n.m.r. spectrum of the same solution showed C₂H₅ signals at τ 8.1 and 8.80, aromatic CH in two groups centered at τ 1.95 and 2.67, and a weak peak at τ -4.9. On dilution with CF₃CO₂H, the

weak peak shifted toward the OH, suggesting exchange.

(b) A solution of 1.38 g. of the salt from part a in 10 ml. of methanol was stirred and cooled to 0° while a solution of 0.27 g. of sodium acetate trihydrate in 5 ml. of methanol was added. The mixture became red immediately, and a precipitate formed in a few minutes. The violet, crystalline precipitate was recrystallized from hexane to give rose-colored needles of *trans*-chloro-*p*-fluorophenylazobis(triethylphosphine)platinum, m.p. 110–113° dec.

Anal. Calcd. for $C_{18}H_{34}ClFN_2P_2Pt$: C, 36.63; H, 5.81; N, 4.75. Found: C, 36.61; H, 5.84; N, 4.62.

Chromatography of the mother liquor on neutral alumina gave both the azo compound and the previously unknown *trans*-chloro-*p*-fluorophenylbis(triethylphosphine)platinum as well-defined bands. The latter crystallized from hexane as white needles, m.p. $104-105^{\circ}$. A mixture with a sample of this compound prepared by the Grignard method melted at $103.5-104.5^{\circ}$. Another chromatographic fraction crystallized from hexane as white flakes, m.p. $194-195^{\circ}$. The infrared spectrum was identical with that of authentic *trans*-di-*p*-fluorophenylbis(triethylphosphine)-platinum(II).

p-Nitrophenylazoplatinum Complex. The preparation of this complex was carried out without isolation of the intermediate *p*-nitrophenylazoplatinum cation.

A mixture of 2.30 g. of *trans*-chlorohydridobis(triethylphosphine)platinum and 1.18 g. of *p*-nitrobenzenediazonium tetrafluoroborate was placed in a 100-ml. flask. When 25 ml. of ethanol was added, a vigorous reaction with much gas evolution occurred and the solution became red-orange. Addition of a solution of 0.33 g. of KOH in 15 ml. of ethanol changed the color to deep red-brown. The solution was filtered to remove KBF₄, and the filtrate was diluted with 150 ml. of water. The red-brown color disappeared on dilution. Extraction of the filtrate with benzene gave a yellow benzene layer. Evaporation under reduced pressure gave a yellow-green oil that partially crystallized on standing.

Chromatography on neutral alumina gave, as the first fraction, pale yellow needles of chloro-*p*-nitro-phenylbis(triethylphosphine)platinum, m.p. 169°.

Anal. Calcd. for $C_{18}H_{34}CINO_2P_2Pt$: C, 36.70; H, 5.82; N, 2.38. Found: C, 36.59; H, 5.86; N, 2.32.

The second fraction on elution with benzene was a green oil which slowly crystallized on standing. The solid dissolved in hexane to give a blue solution from which small, emerald-green crystals of chloro-*p*nitrophenylazobis(triethylphosphine)platinum separated on cooling, m.p. $92-94^{\circ}$. The complex was stable in air but decomposed rapidly in CCl₄ or CHCl₃. *Anal.* Calcd. for C₁₈H₃₄ClN₃O₂P₂Pt: C, 35.03; H,

5.55; N, 6.81. Found: C, 35.27; H, 5.60; N, 7.11.

p-Methoxyphenylplatinum Compound. Reaction of *p*-methoxybenzenediazonium tetrafluoroborate with the platinum hydride in the presence of KOH gave none of the desired *p*-methoxyphenylazo compound. The deep red color of the reaction mixture suggests that it may have formed, but only faintly yellow crystals of chloro-*p*-methoxyphenylbis(triethylphosphine)platinum, m.p. $133-134^{\circ}$, were isolated.

Anal. Calcd. for $C_{19}H_{37}ClOP_2Pt$: C, 39.74; H, 6.49. Found: C, 39.55; H, 6.43.

Authentic Samples of Fluorophenylplatinum Complexes. p-Fluorophenyl Compounds. A solution of 5.02 g. of trans-dichlorobis(triethylphosphine)platinum(II) in 150 ml. of benzene was mixed with 30 ml. of 1.0 M p-fluorophenylmagnesium bromide solution and the mixture was boiled under reflux for 1 hr. The mixture was hydrolyzed with cold dilute hydrochloric acid. Evaporation of the organic layer gave offwhite crystals. Recrystallization from hexane gave 2.9 g. of trans-di-p-fluorophenylbis(triethylphosphine)platinum(II), m.p. 199-200°.

Anal. Calcd. for $C_{24}H_{38}F_2P_2Pt$: C, 46.36; H, 6.16. Found: C, 46.76; H, 6.26.

A solution of 2.5 g. of the di-*p*-fluorophenylplatinum complex in 30 ml. of benzene was treated with anhydrous HCl for 1 min. The solution was evaporated to dryness and the residue was recrystallized from hexane to give white rhombs of *trans*-chloro-*p*fluorophenylbis(triethylphosphine)platinum(II), m.p. $103-104^{\circ}$.

Anal. Calcd. for $C_{18}H_{34}ClFP_2Pt$: C, 38.46; H, 6.10. Found: C, 38.30; H, 6.00.

m-Fluorophenyl Compounds. These complexes were prepared by the procedures described for the *p*-fluorophenyl analogs. The *trans*-di-*m*-fluorophenylbis(triethylphosphine)platinum(II) crystallized from hexane as white flakes, m.p. $200-201^{\circ}$, yield 4.0 g.

Anal. Calcd. for $C_{24}H_{38}F_2P_2Pt$: C, 46.36; H, 6.16. Found: C, 46.72; H, 5.97.

trans-Chloro-*m*-fluorophenylbis(triethylphosphine)platinum(II) crystallized from hexane as long, white needles, m.p. 90–91°.

Anal. Calcd. for $C_{18}H_{34}ClFP_2Pt$: C, 38.46; H, 6.10. Found: C, 38.72; H, 6.06.