# Chemistry of Metal Hydrides. IV.[1] The Synthesis of Platinum and Palladium Cations $[MX(CO)(R_3P)_2]^+$ and $[MX(R_3P)_3]^+$

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**Abstract:** The synthesis is described of the new complexes *trans*-$[PdCl(CO)((C_2H_5)_3P)_2][BF_4]$, $[PdCl((C_2H_5)_3P)_3][B(C_6H_5)_4]$, and $[PtH((C_2H_5)_3P)_3][B(C_6H_5)_4]$ together with a number of related compounds containing complex cations of palladium and platinum. The syntheses involve direct or indirect replacement by carbon monoxide or a tertiary phosphine of chloride from complexes $[MClX((C_2H_5)_3P)_2]$, where X = Cl or H. When X = Cl, the indirect procedure gives first chloride-bridged complexes, such as $[Pd_2Cl_2((C_2H_5)_3P)_4][BF_4]_2$, which have been isolated. The reaction of *cis*-$[PtCl_2((C_2H_5)_3P)_2]$ with sodium tetraphenylborate gives *trans*-$[Pt(C_6H_5)_2((C_2H_5)_3P)_2]$.

There is great current interest[2] in four-coordinate complexes of rhodium(I) and iridium(I), notably $[RhCl(Ph_3P)_3]$ and *trans*-$[IrCl(CO)(Ph_3P)_2]$, both for their activity as homogeneous hydrogenation catalysts and for their oxidative addition reactions. Consequently, our recent discovery[1] of the cation *trans*-$[PtCl(CO)(Et_3P)_2]^+$, isoelectronic with *trans*-$[IrCl(CO)(Ph_3P)_2]$, prompted us to examine synthetic routes to other platinum, palladium, and nickel analogs of the iridium and rhodium systems.

The syntheses described below are based on replacement by a neutral, $\pi$-acceptor ligand such as carbon monoxide or a tertiary phosphine of one halide ion from the readily available complexes $[MX_2(R_3P)_2]$. This can be accomplished in two stages: (i) halide abstraction by boron trifluoride to give isolable, halogen-bridged intermediates, $[M_2X_2(R_3P)_4][BF_4]_2$; and (ii) cleavage of the bridges by the $\pi$-acceptor ligand, or in a single step by the action of the $\pi$-acceptor ligand in the presence of sodium tetraphenylborate. The resulting platinum and palladium complex cations, *trans*-$[MX(CO)(R_3P)_2]^+$ or $[MX(R_3P)_3]^+$, are isoelectronic analogs of *trans*-$[IrCl(CO)(Ph_3P)_2]$ and $[RhCl(Ph_3P)_3]$. The reactions are not completely general for M = Pt, Pd; X = Cl, Br, or I; and R = Et or Ph, but a large number of complexes can be prepared, and their chemistry is currently under investigation for comparison with the iridium and rhodium systems. For M = Ni, only preliminary results[3,4] are available and details will be reported later.

## Results and Discussion

The reaction of the complexes *trans*-$[PdCl_2(R_3P)_2]$, R = Et or Ph, with boron trifluoride at 75° gives the di-$\mu$-chloro-tetrakis(tertiary phosphine)dipalladium(II) tetrafluoroborates, $[Pd_2Cl_2(R_3P)_4][BF_4]_2$. These reactions are similar to those described previously[1,5] for the synthesis of the analogous diplatinum cations, but whereas, with the one exception (X = I and R = Et), the platinum reactions can be extended to bromides and iodides,[3,4] this is not the case for palladium. Even at 120°, *trans*-$[PdBr_2(Et_3P)_2]$ gives no reaction with boron trifluoride, and *trans*-$[PdI_2(Et_3P)_2]$ reacts only slowly according to the equation

$$2[PdI_2(Et_3P)_2] + 2BF_3 \longrightarrow [Pd_2I_4(Et_3P)_2] + 2[Et_3P \cdot BF_3]$$

The difference probably lies in the ease of *trans* to *cis* isomerization of these complexes since for platinum the preferred starting materials[4] are *cis*-$[PtX_2(Et_3P)_2]$ complexes in which the halogen is labilized by the large *trans* effect of the phosphine. For palladium only *trans* complexes have been described in the literature although $[PdCl_2(Et_3P)_2]$ can sometimes be obtained in an unstable *cis* configuration.[4] Moreover, it is known[6] that the equilibrium percentage of *cis* isomer for the complexes $PtX_2(Et_3P)_2$ increases as I < Br < Cl. We therefore suggest that reaction of *trans*-$[PdCl_2(Et_3P)_2]$ with boron trifluoride proceeds *via* a small concentration of *cis* isomer and that this route is not available to the corresponding bromide and iodide.

Cleavage of chloride bridges by carbon monoxide is well known[7] for compounds of the type $[Pt_2Cl_4(R_3P)_2]$, and our recent studies[3] have shown that similar reactions occur with the chloride-bridged complexes, $[Pt_2Cl_2(R_3P)_4][BF_4]_2$, giving stable crystalline salts of the *trans*-$[PtCl(CO)(R_2P)_2]^+$ cations. A similar cleavage is also observed for the analogous chloride-bridged palladium complex, $[Pd_2Cl_2(Et_3P)_4][BF_4]_2$, but palladium carbonyls are generally much less stable than their platinum analogs, and this trend is confirmed in the present case. The equilibrium

$$[Pd_2Cl_2(Et_3P)_4][BF_4]_2 + 2CO \rightleftharpoons 2\,trans\text{-}[PdCl(CO)(Et_3P)_2][BF_4]$$

lies to the right at a carbon monoxide pressure of 1 atm, but although *trans*-chlorocarbonylbis(triethylphosphine)palladium(II) tetrafluoroborate can be isolated, it is very unstable and readily loses carbon monoxide on standing. This is one of very few palladium carbonyl derivatives so far reported and appears to represent a

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[1] For Part III see H. C. Clark, K. R. Dixon, and W. J. Jacobs, *J. Am. Chem. Soc.*, 90, 2259 (1968).

[2] See, for example J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc., A*, 1711 (1966), and references therein.

[3] H. C. Clark, K. R. Dixon, and W. J. Jacobs, *Chem. Commun.*, 93 (1968).

[4] H. C. Clark, K. R. Dixon, and W. J. Jacobs, unpublished observations.

[5] P. M. Druce, M. F. Lappert, and P. N. K. Riley, *Chem. Commun.*, 486 (1967).

[6] J. Chatt and R. G. Wilkins, *J. Chem. Soc.*, 525 (1956).

[7] J. Chatt, N. P. Johnson, and B. L. Shaw, *ibid.*, 1662 (1964).

**Table I.** Characterization Data

| Compound[a] | Color | Mp, °C | Recrystn solvent | %C calcd (found) | %H calcd (found) | Infrared (Nujol mulls), $cm^{-1}$ | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | $\nu$(M–X) | $\nu$(M–P) | $\nu$(C≡O) | $\nu$(Pt–H) | Other |
| *trans*-$[PdCl_2(Et_3P)_2]$[d] | Yellow | 141.5–142.5<br>(139[d]) | $C_2H_5OH$ | | | 356 m | 413 m | | | |
| *trans*-$[PdBr_2(Et_3P)_2]$[d] | Yellow | 138–139<br>(132[d]) | $C_2H_5OH$ | 28.7<br>(28.9) | 6.0<br>(5.6) | <250 | 415 m | | | |
| *trans*-$[PdI_2(Et_3P)_2]$[d] | Orange | 141–142<br>(138[d]) | $C_2H_5OH$ | 24.2<br>(24.6) | 5.1<br>(5.3) | <250 | 410 m | | | |
| *trans*-$[PdCl_2(Ph_3P)_2]$[d] | Yellow | ~250 dec | Toluene | | | 360 m | 440 m | | | |
| *trans*-$[PdBr_2(Ph_3P)_2]$ | Orange | ~250 dec | Toluene | 54.7<br>(54.7) | 3.8<br>(3.8) | <250 | 432 m | | | |
| *trans*-$[PdI_2(Ph_3P)_2]$ | Red | ~250 dec | Toluene | 48.9<br>(48.6) | 3.4<br>(3.3) | <250 | 430 m | | | |
| $[Pd_2Cl_2(Et_3P)_4][BF_4]_2$ | Yellow | ~200 dec | $CH_3OH$–<br>$(C_2H_5)_2O$ | 31.0<br>(31.3) | 6.5<br>(6.6) | 290 wb | 440 w<br>425 m | | | |
| $[Pd_2Cl_4(Et_3P)_2]$[e] | Red | 231–233<br>(230 ) | $C_2H_5OH$ | 24.4<br>(24.8) | 5.1<br>(5.2) | 358 m<br>285 wb | 435 m | | | |
| $[Pd_2I_4(Et_3P)_2]$ | Red | 194.5–196 | $(CH_3)_2CO$ | 15.1<br>(15.5) | 3.2<br>(3.0) | <250 | 423 m | | | |
| $[Pd_2Cl_2(Ph_3P)_4][BF_4]_2$ | Yellow | ~250 dec | $CH_2Cl_2$–<br>$CHCl_3$ | 57.5<br>(58.1) | 4.0<br>(4.0) | 300 mb | 445 m<br>425 m | | | |
| *trans*-$[PdCl(CO)(Et_3P)_2][BF_4]$ | Yellow | Dec | See Exptl. | 31.7<br>(31.7) | 6.1<br>(6.5) | 330 w | 405 w | 2140 (mull) vs<br>2130 ($CHCl_3$) vs | | 479 s |
| $[PdCl(Et_3P)_3][BPh_4]$ | Yellow | 136–138 dec<br>*in vacuo* | $(CH_3)_2CO$–<br>$(C_2H_5)_2O$ | 61.8<br>(61.8) | 8.0<br>(8.0) | 290 wb | 430 sh<br>410 m | | | |
| *trans*-$[PdCl(Et_3P)_2(Ph_3P)][BPh_4]$ | Yellow | ~140 dec<br>*in vacuo* | $(CH_3)_2CO$–<br>$(C_2H_5)_2O$ | 67.6<br>(67.3) | 6.8<br>(7.1) | 300 wb | 440 w<br>420 w | | | |
| $[PtCl(Et_3P)_3][BPh_4]$ | Colorless | 176.5–177.5<br>*in vacuo* | $(CH_3)_2CO$–<br>$(C_2H_5)_2O$ | 55.8<br>(55.9) | 7.3<br>(7.5) | 280 wb | 443 w<br>415 m | | | |
| $[PtH(Et_3P)_3][BPh_4]$ | Colorless | 133–134<br>*in vacuo* | $(CH_3)_2CO$–<br>$(C_2H_5)_2O$ | 58.0<br>(58.1) | 7.7<br>(7.8) | | 440 w<br>421 m<br>342 mb | | 2126 s | |
| $[PtH(Ph_3P)_3][BPh_4]$ | Colorless | | | | | | 425 wb | | 2110 w[b] | |
| *trans*-$[PtH(CO)(Et_3P)_2][BPh_4]$ | Colorless | 115–117 dec<br>*in vacuo* | $(CH_3)_2CO$–<br>$(C_2H_5)_2O$ | 57.0<br>(57.0) | 6.6<br>(6.7) | | 400 mb | 2043 vs[c] | 2162 vs[c] | 465 m |
| *trans*-$[PtPh_2(Et_3P)_2]$[f] | Colorless | 177–181<br>(176–180[f]) | $C_2H_5OH$ | 49.2<br>(48.6) | 6.9<br>(6.4) | | 408 m | | | 498 w |

[a] Previous reports. [b] Reference 14 gives 2112 $cm^{-1}$ for the corresponding $BF_4^-$ salt. [c] Reference 12 gives 2222 $cm^{-1}$ for the corresponding $ClO_4^-$ salt. [d] Reference 22. [e] F. G. Mann and D. Purdie, *J.Chem. Soc.*, 873 (1936). [f] J. Chatt and B. L. Shaw, *ibid.*, 4020 (1959).

new type, other examples being largely confined to compounds[8–10] of the types $[Pd(CO)X_2]_n$, $[Pd(CO)X_3]^-$, and $[Pd_2(CO)_2Cl]_n$.

As noted in the introduction, the above reactions represent a two-stage substitution of halide by a $\mu$-acceptor ligand. The corresponding single-stage substitution is exemplified by the following reactions.

$$[MCl_2(Et_3P)_2] + Et_3P + NaBPh_4 \longrightarrow [MCl(Et_3P_3)][BPh_4] + NaCl \quad (1)$$

These proceed easily and stoichiometrically in tetrahydrofuran for M = Pt or Pd and probably also for M = Ni.[4] The second chloride is not displaced even under reflux. Table I lists some typical products from this type of reaction, and other examples have been reported by Grim, Keiter, and McFarlane[11] and by Church and Mays.[12] The latter authors used carbon monoxide in the presence of sodium perchlorate and, in contrast to our results with tertiary phosphines and sodium tetraphenylborate, found that halide displacement reactions proceeded only with complexes of platinum and not with complexes of palladium or nickel.

Reactions of type 1 appear to be fairly general, but there can be difficulties with the larger and less basic ligands such as triphenylphosphine. For example, tris(tertiary phosphine) metal cations containing both triethyl- and triphenylphosphine preferentially eliminate the larger ligand (reactions 2 and 3 below) and a reaction similar to eq 1 did not give $[PdCl(Ph_3P)_3][BPh_4]$ under mild conditions.

Another limitation on the use of this procedure is the possibility of phenyl-transfer reactions. Thus *cis*-$[PtCl_2(Et_3P)_2]$ and sodium tetraphenylborate under reflux in tetrahydrofuran give an interesting and unusual reaction which proceeds essentially stoichiometrically according to the equation

$$cis\text{-}[PtCl_2(Et_3P)_2] + 2NaBPh_4 \longrightarrow trans\text{-}[PtPh_2(Et_3P)_2] + 2NaCl + 2BPh_3$$

This may be compared with the reaction of mercuric chloride with sodium tetraphenylborate to give phenylmercuric chloride.[13]

Hydridotris(triethylphosphine)platinum(II) tetraphenylborate is obtained when *trans*-$[PtHCl(Et_3P)_2]$ is used in reaction 1 instead of a dihalo complex. It is

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(8) R. J. Irving and E. A. Magnusson, *J. Chem. Soc.*, 2283 (1598).
(9) J. S. Anderson, *Quart. Rev.* (London), 1, 331 (1947).
(10) E. O. Fischer and A. Vogler, *J. Organometal. Chem.*, **3**, 161 (1965).
(11) S. O. Grim, R. L. Keiter, and W. McFarlane, *Inorg. Chem.*, **6**, 1133 (1967).
(12) M. J. Church and M. J. Mays, *Chem. Commun.*, 435 (1968).
(13) G. E. Coates, "Organometallic Compounds," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1960.

particularly interesting as the first alkylphosphine analog of the $[PtH(Ph_3P)_3]^+$ cation[14] especially as its high solubility makes it suitable for nmr study. The hydridic proton nmr resonance of the $[PtH(Et_3P)_3]^+$ cation is the expected doublet of triplets due to coupling with *trans*- and *cis*-phosphorus, respectively. There are also side bands due to coupling with $^{195}Pt$ (34% abundance). Table II compares the various parameters with those reported previously[15] for *trans*-$[PtHCl(Et_3P)_2]$ and *trans*-$[PtH(CN)(Et_3P)_2]$.

Table II. Nmr Parameters for $[PtH(Et_3P)_3]^+$

| Compound | Chemical shift ($\tau$) | Coupling constants, cps<br>H–P$_{trans}$ | <br>H–P$_{cis}$ | <br>H–Pt |
|---|---|---|---|---|
| *trans*-$[PtHCl(Et_3P)_2]$[a] | 26.8 | | 14.5 | 1275 |
| *trans*-$[PtH(CN)(Et_3P)_2]$[a] | 17.6 | | 15.6 | 778 |
| $[PtH(Et_3P)_3]^+$ | 15.9 | 157 | 15 | 788 |

[a] Reference 15.

The effect of the positive charge in reducing electron density in the Pt–H bond is seen to be closely similar to the effect of a strongly electronegative *trans* ligand such as cyanide.

The nmr spectrum of the $[PtH(Et_3P)_3]^+$ cation shows that phosphine exchange is slow on the nmr time scale, but, nevertheless, the tris(tertiary phosphine)metal cations are potentially very labile systems. For example, they are almost certainly intermediates in the catalysis by traces of tertiary phosphine of *cis–trans* isomerization of complexes, $PtX_2(R_3P)_2$.[13] This lability is further demonstrated by the quantitative displacement reactions

$$trans\text{-}[PdCl_2(Ph_3P)_2] + 3Et_3P + NaBPh_4 \longrightarrow [PdCl(Et_3P)_3][BPh_4] + NaCl + 2Ph_3P \quad (2)$$

$$cis\text{-}[PtCl_2(Ph_3P)_2] + 2Et_3P \longrightarrow cis\text{-}[PtCl_2(Et_3P)_2] + 2Ph_3P \quad (3)$$

Reaction 3 is not reversed even by a large excess of triphenylphosphine.

## Experimental Section

Reactions 1 below were conducted in evacuated, thick-walled, Pyrex glass tubes (~50-ml capacity) and reactions 3–6 were conducted in a nitrogen atmosphere. Tetrahydrofuran was dried and deoxygenated by reflux over potassium benzophenone ketyl. Except as indicated below, the products were stable and were isolated and purified in the atmosphere. The solvents used for recrystallizations are included in Table I. Where solvent pairs were used, the second solvent was added dropwise to a concentrated solution of the complex in the first solvent until crystallization began.

The $^1H$ nmr spectrum of *trans*-$[PdCl(CO)(Et_3P)_2][BF_4]$ was recorded under a carbon monoxide pressure of 6 atm. The hydridic proton nmr resonance of $[PtH(Et_3P)_3][BPh_4]$ was recorded in methylene chloride solution on a Varian HA 100 spectrometer and the chemical shift measured relative to the solvent. The molecular weight of $[Pd_2I_4(Et_3P)_2]$ was measured in benzene solution using a Hitachi Perkin-Elmer Model 115 osmometer. Other general techniques and instrumentation have been described previously.[1]

Analytical data are included in Table I together with infrared absorptions other than those due to internal vibrations of ligands or anions. The complexes were characterized by the clearly defined stoichiometry of many of the reactions, together with infrared spectra and, where appropriate, the relative integrated intensities of ethyl and phenyl resonances in the $^1H$ nmr spectra. *cis* and *trans* isomers were differentiated where necessary by $^1H$ nmr and infrared criteria as established previously.[1] While assignments of configuration and metal-phosphorus infrared stretching modes in complexes of triethylphosphine can be made with confidence, the corresponding assignments for complexes of triphenylphosphine are tentative.

Complexes of platinum(II) were prepared as previously described.[16–18] Complexes of palladium(II) were prepared by methods analogous to those previously described[19–22] but using solutions of tetrahalopalladites obtained by solution of $PdCl_2$ in water containing a large excess of the appropriate sodium halide. Use of sodium iodide in this procedure caused some reduction to palladium metal with consequent loss of yield, but otherwise yields of 95–100% were obtained. $[PdBr_2(Ph_3P)_2]$ and $[PdI_2(Ph_3P)_2]$ have not been reported previously.

**1. Reactions of Complexes $[PdX_2(R_3P)_3]$ with Boron Trifluoride.** (a) *trans*-$[PdCl_2(Et_3P)_2]$ (1.0 g, 2.4 mmoles) was shaken with boron trifluoride (1.5 g, 22 mmoles) in dry chloroform (5 ml) at 75° for 20 hr. An orange oil precipitated. Volatile materials were removed under vacuum at 25° and the residues extracted with methanol (15 ml). Dropwise addition of diethyl ether (20 ml) to the extract gave $[Pd_2Cl_2(Et_3P)_4][BF_4]_2$ (0.42 g, 0.45 mmole) as yellow needles whose molar conductivity in $10^{-3}$ *M* solution in nitromethane was 177 $ohm^{-1}$ $cm^2$. The mother liquors contained further small quantities of this complex together with unreacted *trans*-$[PdCl_2(Et_3P)_2]$ and also $[Pd_2Cl_4(Et_3P)_2]$ (0.04 g, 0.07 mmole).

(b) *trans*-$[PdBr_2(Et_3P)_2]$ (0.25 g, 0.50 mmole) showed no evidence of reaction with boron trifluoride (1.4 g, 21 mmoles) after 60 hr at 120° in dry chloroform (5 ml).

(c) *trans*-$[PdI_2(Et_3P)_2]$ (0.24 g, 0.40 mmole) was shaken with boron trifluoride (1.4 g, 21 mmoles) in dry chloroform (5 ml) at 120° for 60 hr. After removal of volatile materials under vacuum at 120°, the solid residues were thoroughly extracted with boiling light petroleum and then washed with methanol. $[Pd_2I_4(Et_3P)_2]$ (0.07 g, 0.07 mmole; mol wt: calcd, 957; found, 935) remained as a residue, and evaporation of the petroleum extract gave *trans*-$[PdI_2(Et_3P)_2]$ (0.14 g, 0.24 mmole).

(d) *trans*-$[PdCl_2(Ph_3P)_2]$ (0.20 g, 0.28 mmole) was heated with boron trifluoride (1.5 g, 22 mmoles) in dry toluene (5 ml) at 120° for 24 hr. Volatile materials were removed under vacuum at 25° and the residues extracted with small volumes of nitromethane. Addition of diethyl ether to this extract gave a yellow precipitate which was reextracted with nitromethane. Addition of diethyl ether to the extract gave $[Pd_2Cl_2(Ph_3P)_4][BF_4]_2$ (0.08 g, 0.05 mmole) as a yellow powder whose molar conductivity in $10^{-3}$ *M* solution in nitromethane was 167 $ohm^{-1}$ $cm^2$. The residue from these extracts was *trans*-$[PdCl_2(Ph_3P)_2]$ (0.05 g, 0.07 mmole).

(e) *trans*-$[PdBr_2(Ph_3P)_2]$ and *trans*-$[PdI_2(Ph_3P)_2]$ gave more complex reactions with boron trifluoride, the products of which are still under investigation.

**2. Preparation of *trans*-$[PdCl(CO)(Et_3P)_2][BF_4]$.** A suspension of $[Pd_2Cl_2(Et_3P)_4][BF_4]_2$ (0.20 g, 0.21 mmole) in chloroform (5 ml) was stirred under carbon monoxide (1 atm) until solution was complete (15–20 hr). All subsequent operations were also carried out in a carbon monoxide atmosphere, and all solvents were presaturated with carbon monoxide. A small quantity of palladium metal was removed by filtration and the filtrate added rapidly dropwise to cyclohexane (100 ml). *trans*-$[PdCl(CO)(Et_3P)_2][BF_4]$ (0.18 g, 0.37 mmole) was obtained as a yellow precipitate and purified by several repetitions of the sequence; solution in chloroform, filtration, addition of filtrate to cyclohexane.

This carbonyl is very unstable and readily loses carbon monoxide giving $[Pd_2Cl_2(Et_3P)_4][BF_4]_2$ which precipitates as an oil from chloroform solution. Even the solid carbonyl loses carbon monoxide slowly, and it is probable that all samples contained traces of dimer, as indicated by weak bands in the infrared at 440 and 425 $cm^{-1}$. This impurity would have very little effect on analytical data.

**3. Preparation of "Tris(tertiary phosphine)" Complexes.** (a) **$[PdCl(Et_3P)_3][BPh_4]$.** Triethylphosphine (0.16 ml, 0.11 mmole) as a solution in 10 ml of dry tetrahydrofuran was added dropwise with stirring to a solution of *trans*-$[PdCl_2(Et_3P)_2]$ (0.20 g, 0.48 mmole) with sodium tetraphenylborate (0.33 g, 0.96 mmole) in 10 ml of tetrahydrofuran. The solution became cloudy almost immediately,

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[14] F. Cariati, R. Ugo, and F. Bonati, *Inorg. Chem.*, **5**, 1128 (1966).

[15] J. Powell and B. L. Shaw, *J. Chem. Soc.*, 3879 (1965).

[16] J. Chatt and B. L. Shaw, *ibid.*, 5075 (1962).

[17] K. A. Jensen, *Z. Anorg. Allgem. Chem.*, **229**, 238 (1936).

[18] J. C. Bailar, Jr., and H. Itatani, *Inorg. Chem.*, **4**, 1618 (1965).

[19] F. G. Mann and D. Purdie, *J. Chem. Soc.*, 1549 (1935).

[20] J. Chatt and F. G. Mann, *ibid.*, 1622 (1939).

[21] G. Calvin and G. E. Coates, *ibid.*, 2008 (1960).

[22] G. Booth, *Advan. Inorg. Chem. Radiochem.*, **6**, 1 (1964).

but stirring was continued for 20 hr at 25° before removal of solvent and excess triethylphosphine under vacuum. The residues were extracted with methylene chloride, followed by acetone, followed by water. Evaporation of the organic extracts and addition of silver nitrate to the acidified aqueous extract gave $[\mathrm{PdCl(Et_3P)_3}][\mathrm{BPh_4}]$ (0.39 g, 0.48 mmole) from the methylene chloride, sodium tetraphenylborate (0.15 g, 0.44 mmole) from the acetone, and silver chloride (0.07 g, 0.49 mmole) from the water.

A second reaction under reflux for 5 hr gave similar results.

**(b)** ***trans*-$[\mathrm{PdCl(Et_3P)_2(Ph_3P)}][\mathrm{BPh_4}]$.** By the same procedure triphenylphosphine (0.127 g, 0.48 mmole), *trans*-$[\mathrm{PdCl_2(Et_3P)_2}]$ (0.200 g, 0.5 mmole), and sodium tetraphenylborate (0.166 g, 0.5 mmole) gave silver chloride (0.068 g, 0.5 mmole) and *trans*-$[\mathrm{PdCl(Et_3P)_2(Ph_3P)}][\mathrm{BPh_4}]$ (0.48 g, 0.5 mmole). This complex was somewhat air sensitive, particularly in solution, and was best handled in a nitrogen atmosphere.

(c) **$[\mathrm{PtCl(Et_3P)_3}][\mathrm{BPh_4}]$.** By the same procedure triethylphosphine (0.08 ml, 0.54 mmole) and *cis*-$[\mathrm{PtCl_2(Et_3P)_2}]$ (0.201 g, 0.40 mmole) gave silver chloride (0.057 g, 0.40 mmole) and $[\mathrm{PtCl(Et_3P)_3}][\mathrm{BPh_4}]$ (0.365 g, 0.40 mmole).

**(d) $[\mathrm{PtH(Et_3P)_3}][\mathrm{BPh_4}]$.** By the same procedure triethylphosphine (0.07 ml, 0.44 mmol) and sodium tetraphenylborate (0.149 g, 0.44 mmole) gave silver chloride (0.062 g, 0.43 mmole) and $[\mathrm{PtH(Et_3P)_3}][\mathrm{BPh_4}]$ (0.38 g, 0.44 mmole).

(e) **$[\mathrm{PtH(Ph_3P)_3}][\mathrm{BPh_4}]$.** By the same procedure triphenylphosphine (0.077 g, 0.3 mmole), *trans*-$[\mathrm{PtHCl(Ph_3P)_2}]$ (0.221 g, 0.3 mmole), and sodium tetraphenylborate (0.100 g, 0.3 mmole) gave silver chloride (0.039 g, 0.3 mmole) and $[\mathrm{PtH(Ph_3P)_3}][\mathrm{BPh_4}]$ (0.39 g, 0.3 mmole).

4. **Preparation of *trans*-$[\mathrm{PtH(CO)(Et_3P)_2}][\mathrm{BPh_4}]$.** A procedure similar to 3d above but using carbon monoxide (1 atm) instead of triethylphosphine gave *trans*-$[\mathrm{PtH(CO)(Et_3P)_2}][\mathrm{BPh_4}]$ (0.321 g, 0.412 mmole).

5. **Ligand-Exchange Reactions.** (a) A procedure similar to 3a above but using triethylphosphine (0.2 ml, 1.4 mmole), *trans*-$[\mathrm{PdCl_2(Ph_3P)_2}]$ (0.200 g, 0.285 mmole), and sodium tetraphenylborate (0.098 g, 0.286 mmole) gave silver chloride (0.040 g, 0.279 mmole) and a methylene chloride extract. Evaporation of this extract to small bulk followed by addition of diethyl ether gave $[\mathrm{PdCl(Et_3P)_3}][\mathrm{BPh_4}]$ (0.222 g, 0.258 mmole). *Anal.* Calcd for $\mathrm{C_{42}H_{65}BClP_3Pd}$: C, 61.8; H, 8.0. Found: C, 61.7; H, 8.2. The mother liquor contained triphenylphosphine (0.148 g, 0.564 mmole), identified by infrared spectroscopy and melting point with a genuine sample).

(b) A procedure similar to 3a above but using triethylphosphine (0.05 ml, 0.34 mmole) and *cis*-$[\mathrm{PtCl_2(Ph_3P)_2}]$ (0.107 g, 0.137 mmole) gave a light petroleum extract containing triphenylphosphine (0.072 g, 0.274 mmole). The residue was *cis*-$[\mathrm{PtCl_2(Et_3P)_2}]$ (0.068 g, 0.135 mmole). Both products were identified by infrared spectroscopy and mixture melting points with genuine samples.

A similar reaction using triphenylphosphine (0.506 g, 1.9 mmoles) and *cis*-$[\mathrm{PtCl_2(Et_3P)_2}]$ (0.093 g, 0.185 mmole) gave quantitative recovery of starting materials.

6. **Reaction of *cis*-$[\mathrm{PtCl_2(Et_3P)_2}]$ with $\mathrm{NaBPh_4}$.** *cis*-$[\mathrm{PtCl_2(Et_3P)_2}]$ (0.211 g, 0.420 mmole) was heated under reflux in 15 ml of dry tetrahydrofuran with $\mathrm{NaBPh_4}$ (0.288 g, 0.842 mmole) for 40 hr. Solvent was removed under vacuum and the residue extracted with methylene chloride, washed with acetone, and extracted with water.

Addition of silver nitrate to the acidified aqueous extract gave silver chloride (0.118 g, 0.824 mmole).

The methylene chloride extract was evaporated and the resulting residue reextracted with cyclohexane Evaporation of the cyclohexane followed by washing of the solid obtained with small volumes of methanol left *trans*-$[\mathrm{PtPh_2(Et_3P)_2}]$ (0.229 g, 0.39 mmole) as a white residue.

A repeat reaction, in which the reaction mixture after removal of tetrahydrofuran was heated under vacuum at 70°, gave a white sublimate with infrared spectrum identical with that reported[23] for triphenylboron.

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[23] D. W. A. Sharp and N. Sheppard, *J. Chem. Soc.*, 674 (1957).

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# Kinetic Studies of the Reduction of Monosubstituted Iron(III) Complexes by Europium(II) and Chromium(II) in Acidic Solution[1]

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**Abstract:** Rates have been measured for the oxidation–reduction reactions occurring between various Fe(III) complexes of the type $(\mathrm{H_2O})_5\mathrm{FeX}^{2+}$ and $\mathrm{Cr}^{2+}$ and $\mathrm{Eu}^{2+}$. The order of reduction rates differs, being $\mathrm{Br} > \mathrm{Cl} > \mathrm{F}$ for Cr(II) reductions and the reverse for Eu(II). The Cr(II) reactions proceed by inner-sphere mechanisms, with transfer of the bridging ligand. Indirect arguments for Eu(II) are advanced in favor of inner-sphere mechanisms, but ligand transfer probably does not take place owing to the greater substitution lability of Eu(III) compared to Fe(II). Some complexation equilibria and rates are evaluated, notably for $\mathrm{FeNCO}^{2+}$. The products of the reduction of this complex by $\mathrm{Cr}^{2+}$ have also been examined.

This paper represents a further report of work related to the question of the details of one-equivalent oxidation–reduction reactions. A number of studies on related reactions have been published recently.[2,3]

One question of current interest is whether particular electron-transfer reactions proceed by either inner- or

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[1] (a) Work was performed in the Ames Laboratory, under the auspices of the U. S. Atomic Energy Commission. (b) Based on the Ph.D. thesis of D. W. C., Iowa State University, Ames, Iowa; (c) NASA graduate trainee, 1967–1968.

[2] D. W. Carlyle and J. H. Espenson, *J. Am. Chem. Soc.*, **90**, 2272 (1968), and references cited therein.

[3] Recent reviews of this area have appeared: (a) N. Sutin, *Ann. Rev. Phys. Chem.*, 17, 119 (1966); (b) *Accounts Chem. Res.*, 1, 225 (1968); (c) A. G. Sykes, *Advan. Inorg. Chem. Radiochem.*, 10, 153 (1968).