

unique one, is a hydrogen bond between the coordinated water molecule and the nitrogen of a cyanide.

Likewise the values of k_{-3} appear reasonable in terms of the interchange processes represented by reaction IIb. The approximate constancy of k_{-3} (and of the associated activation parameters) for the three $M(CN)_6^{3-}$ ions is noted in Tables I and II, and these values are *ca.* 10 times larger than that for k_{-3} in the case of $Fe(CN)_6^{4-}$. Similar electrostatic and polarization arguments are applicable.

The approximate constancy for the $M(CN)_6^{3-}$ reactions of the quantity $k_{\ddagger} = (k_3 + k_{-3})K_{os}$ suggests approximately constant values of k_3 for each reaction as well. The very reasonable assumption is made that K_{os} has approximately the same value for each $M(CN)_6^{3-}$ reaction, based on the concept that outer-sphere association should be quite non-specific for reactants of similar charge types, formulas, and structures.

Consequently, as is often the case in octahedral substitutions, the reaction rates are "dissociatively controlled." That is, the transition state for reaction IIb, although it contains $M(CN)_6^{3-}$, reflects primarily cobalt-water bond breaking. That k_3 for $M(CN)_6^{3-}$ should be $> \sim 10k_3$ for $Fe(CN)_6^{4-}$ is possibly explained by the greater difficulty in dissociation of the water molecule which experiences not only the cobalt-oxygen bond but also hydrogen bonding (or other association) to the entering ferrocyanide.

Mechanistic Comparisons. It appears helpful to consider the results and conclusions of the present study in comparison with certain published results on mechanisms assigned to octahedral substitutions. The most pertinent studies relate to alkylcobaloximes^{5,6} and to other alkyl complexes of related macrocyclic ligands,⁹ although note must be taken of the recent study of the anation of $(H_2O)_5RhCl^{2+}$ by Cl^- .²²

These authors consider the mechanisms given in Schemes I and II, which often are indistinguishable, and succeed in rejecting II in this case.

The usual situation for the reactions of alkylaquocobalt complexes is that the value of k_{obsd} is a linear function of the concentration of the entering ligand L, as in the $M(CN)_6^{3-}$ reactions here. That being the case, relatively few unambiguous distinctions can be made on that basis alone. In the fewer instances in which curvature of the plots of k_{obsd} vs. [L] was noted the interpretations have varied. Thus the first study^{9a} of the substitution of the $RCo(dpn)H_2O^{+23}$ by various entering groups in acetone containing 1% water was interpreted in terms of the limiting SN1 mechanism of Scheme I. More recently the Me and Et derivatives of the same compound have been studied in aqueous solution.^{9b} In this case the results clearly are not consistent with this mechanism in that the resulting values of the k_1 parameter of Scheme I vary for the different entering ligands. These authors thus assign their reactions to the outer-sphere complexation process of Scheme II, as we also have done in this instance.

Acknowledgment. We are grateful to Professor G. Gordon and Mr. R. Silverman for helpful discussions.

Registry No. $C_2H_5Co(dmgh)_2H_2O$, 26025-30-9; $Co(CN)_6^{3-}$, 14897-04-2; $Fe(CN)_6^{3-}$, 13408-62-3; $Cr(CN)_6^{3-}$, 14875-14-0; $Fe(CN)_6^{4-}$, 13408-63-4.

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(23) The group R represents various alkyls and aryls, and dpn is the monoanion of 1,3-bis(biacetylmonoximeimine), a planar, tetradentate ligand, similar to $(dmgh)_2$, whose structure is depicted in ref 9a.

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Formation and Properties of Some New σ -Aryl Derivatives of Iridium(I) and Iridium(III)

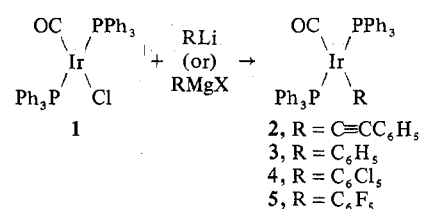
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Received August 9, 1973

Several square-planar complexes of the type $Ir(Ar)(CO)(PPh_3)_2$ ($Ar = C_6H_5, C_6F_5, C_6Cl_5$) have been prepared from reactions of $IrCl(CO)(PPh_3)_2$ and appropriate aryllithium reagents or arylmagnesium halides. The σ -pentahaloaryl complexes were found to undergo reversible oxidative addition reactions with hydrogen chloride to form six-coordinate iridium(III) complexes. An attempted exchange reaction of $Ir(\sigma-C_6F_5)(CO)(PPh_3)_2$ and diphenylmethylphosphine has resulted in the formation of σ -pentafluorophenyltris(diphenylmethylphosphine)iridium(I).

Since the first report of the preparation¹ and formulation² of chlorocarbonylbis(triphenylphosphine)iridium(I) (**1**), an enormous amount of interest concerning the properties and reactivities of various halogen and phosphine analogs of (**1**) has been generated.³⁻⁶ It is also now well established that both phosphine and carbonyl ligands tend to facilitate the stabilization of σ -bonded organic derivatives of transition metals.⁷ It is therefore surprising that, up to the present

time, there has been only one report of any organometallic derivatives of these iridium(I) complexes, namely, the formation of σ -phenylethynylcarbonylbis(triphenylphosphine)iridium(I) (**2**).⁸



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(4) J. P. Collman and W. R. Roper, *Advan. Organometal. Chem.*, **7**, 53 (1968).

(5) J. P. Collman, *Accounts Chem. Res.*, **1**, 136 (1968).

(6) J. Halpern, *Accounts Chem. Res.*, **3**, 386 (1970).

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(8) R. Nast and L. Dahlenburg, *Chem. Ber.*, **105**, 1456 (1972).

In conjunction with our continuing program concerning the formation, stabilization and reactions of σ -bonded organo-(transition metal) compounds, three new σ -aryl derivatives of $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ (**1**) have been prepared. σ -Phenylcarbonylbis(triphenylphosphine)iridium(I) (**3**) was obtained as a light orange solid in 52% yield from a reaction between **1** and phenyllithium in benzene-ethyl ether solution. A reaction between pentachlorophenylmagnesium chloride and **1** in tetrahydrofuran solution resulted in the formation of σ -pentachlorophenylcarbonylbis(triphenylphosphine)iridium(I) (**4**) in 60% yield. σ -Pentafluorophenylcarbonylbis(triphenylphosphine)iridium(I) (**5**) was likewise prepared in 36% yield when pentafluorophenylmagnesium bromide and **1** were allowed to react in tetrahydrofuran solution. The optimum yield of **5** was obtained when a 2.2:1 molar ratio of pentafluorophenylmagnesium bromide to **1** was used in this reaction.

All three of these new organometallic derivatives of **1** are soluble in most polar organic solvents, including benzene, tetrahydrofuran, chloroform, and methanol. The perhaloaryl complexes **4** and **5**, as might be expected, are more stable in air than is the σ -phenyl analog **3**; however, **3** can be handled in air for short periods. The σ -pentachlorophenyl derivative **4** showed no sign of decomposition in the solid state for a period of 2 months under nitrogen, while the σ -pentafluorophenyl analog **5** did slowly decompose to a purple-green solid during this same period.

All attempts to prepare a σ -methyl derivative of **1** have thus far been unsuccessful. Neither methylolithium nor methylmagnesium chloride resulted in a displacement reaction, and starting materials were largely recovered in most runs. Further studies on the formation and properties of σ -alkyl derivatives of **1** are currently in progress.

An initial study on the comparative reactivities of these new σ -arylium complexes relative to **1** has also been undertaken. Both **4** and **5** form hydrogen chloride oxidative addition products when concentrated hydrochloric acid is allowed to react with benzene solutions of these complexes. The σ -pentafluoro complex **5** reacts immediately, as does the parent complex **1**, while the σ -pentachlorophenyl analog **4** requires a longer period of time (*ca.* 12 hr) to afford a complete reaction. This result is very probably due to the enhanced steric requirements imposed by the bulky pentachlorophenyl group on oxidative addition.^{9,10} These reactions can be followed visually by the disappearance of the yellow color of the iridium(I) complex or spectrophotometrically by observing the change in the carbonyl stretching frequencies. When the hydrogen chloride addition product of **5** was heated in ethanol, hydrogen chloride was readily removed to regenerate **4** in high yield. Once the cream-colored HCl adducts of **4** and **5** were formed and were isolated from solution, neither showed signs of reductive elimination of hydrogen chloride in the solid state.

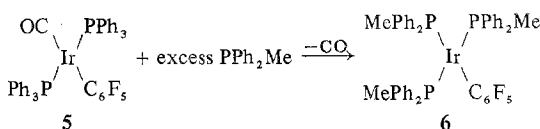
The $\nu(\text{Ir-H})$ absorption peaks at 2236 and 2234 cm^{-1} for the HCl adducts of **4** and **5**, respectively, are consistent with a single isomer being formed in each case and with the hydrogen atom being trans to either the halogen or the pentahaloaryl substituent (Table I). It has previously been shown¹¹ that cis and/or trans addition of hydrogen chloride to **1** can occur, depending on the solvent system, and therefore definitive structural assignments of these HCl adducts must await the results of far-infrared and X-ray diffraction studies.

Table I. Infrared Spectral Data of Some New Iridium(I) and Iridium(III) Complexes^a

Complex	$\nu(\text{CO}), \text{cm}^{-1}$	$\nu(\text{Ir-H}), \text{cm}^{-1}$
$\text{IrCl}(\text{CO})(\text{Ph}_3\text{P})_2$ (1)	1955 s	
$\text{Ir}(\sigma\text{-C}_6\text{H}_5)(\text{CO})(\text{Ph}_3\text{P})_2$ (3)	1939 s	
$\text{Ir}(\sigma\text{-C}_6\text{Cl}_5)(\text{CO})(\text{Ph}_3\text{P})_2$ (4)	1986 w	
$\text{Ir}(\sigma\text{-C}_6\text{F}_5)(\text{CO})(\text{Ph}_3\text{P})_2$ (5)	1968 s	
$\text{Ir}(\text{H})(\text{Cl})(\sigma\text{-C}_6\text{Cl}_5)(\text{CO})(\text{Ph}_3\text{P})_2$	2015 s	2236 m
$\text{Ir}(\text{H})(\text{Cl})(\sigma\text{-C}_6\text{F}_5)(\text{CO})(\text{Ph}_3\text{P})_2$	2041 s	2234 m

^a Recorded in Nujol mull.

Diphenylmethylphosphine is reported¹² to undergo a phosphine-exchange reaction with **1**, yielding chlorocarbonylbis(diphenylmethylphosphine)iridium(I). Under these same experimental conditions, **5** reacts in an anomalous manner. The σ -pentafluorophenyl complex **5** was found to undergo not only exchange of both triphenylphosphine ligands, but in addition the carbonyl group was displaced as well, forming σ -pentafluorophenyltris(diphenylmethylphosphine)iridium(I) (**6**).



This new trisphosphine complex was characterized by elemental analysis and by spectroscopic means. The absence of a carbonyl stretching frequency in the infrared spectrum of **6** obviously indicates loss of the carbonyl group from **5**. The proton nmr spectrum of **6** in CDCl_3 solution exhibits a triplet ($J = 4$ Hz) centered at τ 8.61. This splitting pattern is characteristic of the methyl signal of two diphenylmethylphosphine ligands when they are trans in a square-planar complex and arises from virtual coupling.^{13,14} A doublet ($J = 9$ Hz) which occurs at τ 7.82 can be assigned to the methyl group of the diphenylmethylphosphine ligand which is trans to the σ -pentafluorophenyl group. This doublet resonance is due to coupling of the methyl protons with the phosphorus atom to which the group is attached. A multiplet resonance which occurs at τ 2.85 is assigned to the aromatic protons.

Select infrared spectral data of these new σ -arylium complexes are summarized in Table I. In both **4** and **5**, the carbonyl stretching frequencies are raised in energy compared to **1**, however, $\nu(\text{CO})$ of the σ -phenyl analog **3** is lowered. These results suggest an increase in the group electronegativity of C_6F_5 and C_6Cl_5 relative to chlorine. This increased electronegativity essentially removes electron density from the iridium atom. The overall effect of a perhaloaryl group as compared to a chloro group is therefore to shift $\nu(\text{CO})$ to a higher frequency in these complexes as a result of diminished back-donation from the metal to antibonding orbitals of the CO ligand. In the case of **5**, apparently the σ -pentafluorophenyl group more effectively labilizes the carbonyl ligand toward substitution by the basic phosphine than does the chloro group in **1**.

The above-mentioned oxidative addition and substitution reactions of these new σ -aryl derivatives of iridium(I) suggest that substantial variations in their reactivities compared to the well-known parent complex **1** can be expected, due both

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to electronic and steric differences. Further studies designed to elucidate these differences are in progress.

Experimental Section

Ethyl ether was purified by initial drying over calcium chloride followed by distillation under nitrogen from the sodium-benzo-phenone radical. Tetrahydrofuran was purified by allowing it to stand over potassium hydroxide pellets for 2 days followed by refluxing and distillation under nitrogen from the sodium-naphthalene radical. Both hexane and benzene were purified by distillation under nitrogen from calcium hydride. Chlorocarbonylbis(triphenylphosphine)iridium(I) was prepared by a literature procedure.¹⁵ Phenyllithium, diphenylmethylphosphine, hexachlorobenzene, and bromopentafluorobenzene were all used as obtained commercially. Infrared spectra were recorded on a Beckmann IR 10 spectrophotometer calibrated vs. polystyrene. Proton nmr spectra were recorded on a Varian A-60 spectrometer. Melting points were recorded on a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts.

Preparation of σ -Phenylcarbonylbis(triphenylphosphine)iridium(I) (3). Chlorocarbonylbis(triphenylphosphine)iridium(I) (390 mg, 0.50 mmol) was suspended in 40 ml of a 70:30 benzene-ethyl ether solution under nitrogen to give a yellow suspension which was cooled to 0°. Phenyllithium (0.55 mmol) was added dropwise with rapid stirring. The color immediately changed from yellow to orange. Stirring was continued for 1 hr while the solution was allowed to warm to room temperature. The reaction mixture was filtered under nitrogen and the residue was washed with ethyl ether. The solvent was removed from the filtrate to yield a light orange solid. Recrystallization of the product from benzene-heptane yielded σ -phenylcarbonylbis(triphenylphosphine)iridium(I), yield 213 mg (52%), mp 159° (sealed tube under N₂).

Anal. Calcd for C₄₃H₃₅IrOP₂: C, 62.84; H, 4.29; Ir, 23.38; O, 1.95; P, 7.54. Found: C, 63.00; H, 4.39; Ir, 23.21; O, 2.00; P, 7.50.

Preparation of σ -Pentachlorophenylcarbonylbis(triphenylphosphine)iridium(I) (4). Pentachlorophenylmagnesium chloride was prepared according to a literature procedure¹⁶ from hexachlorobenzene (0.85 g, 3.0 mmol) and dry magnesium turnings (0.073 g, 3.0 g-atoms) in 25 ml of anhydrous tetrahydrofuran. A crystal of iodine was added and warming was necessary to initiate the reaction. The reaction mixture was allowed to stir for 14 hr during which time it became dark brown. Chlorocarbonylbis(triphenylphosphine)iridium(I) (1.56 g, 2.0 mmol) was added in small portions to the tetrahydrofuran solution of pentachlorophenylmagnesium chloride. The solution was refluxed for 4 hr and then allowed to stir at room temperature for 12 hr. The solvent was removed at reduced pressure and the resulting solid was dissolved in 1.5 ml of benzene and transferred to a hexane-packed column of alumina (5.5% water added, 2.5 cm × 34 cm). Hexane elution removed a mixture of hexachlorobenzene and pentachlorobenzene. A yellow band was eluted with hexane-benzene (1:1). Evaporation of the solvent afforded a yellow solid which upon recrystallization from benzene-heptane afforded 1.20 g of σ -pentachlorophenylcarbonylbis(triphenylphosphine)iridium(I), mp 243° (sealed tube under N₂). The yield was 60%.

Anal. Calcd for C₄₃H₃₀Cl₅IrOP₂: C, 51.95; H, 3.04; Cl, 17.83; Ir, 19.33; O, 1.61; P, 6.23. Found: C, 52.14; H, 3.27; Cl, 18.39; Ir, 18.85; O, 1.70; P, 6.45.

Preparation of σ -Pentafluorophenylcarbonylbis(triphenylphosphine)iridium(I) (5). Pentafluorophenylmagnesium bromide was prepared from bromopentafluorobenzene (1.09 g, 4.4 mmol) and dry magnesium (0.11 g, 4.4 g-atoms) in 15 ml of anhydrous tetrahydrofuran under nitrogen. After the formation of the Grignard reagent (about 2 hr, slight warming necessary), 35 ml of anhydrous tetrahydrofuran was added, and chlorocarbonylbis(triphenylphosphine)iridium(I) (1.56 g, 2.0 mmol) was subsequently added in one portion. The heterogeneous reaction mixture was refluxed for 6 hr, cooled, and

absorbed onto 5 g of alumina while the solvent was removed. The coated alumina was added to a hexane-packed alumina column (5.5% water added, 2.0 cm × 40 cm). Treatment with hexane-benzene (1:1) eluted a yellow band of σ -pentafluorophenylcarbonylbis(triphenylphosphine)iridium(I), and subsequent treatment with benzene eluted unreacted chlorocarbonylbis(triphenylphosphine)iridium(I). The product (5) was recrystallized from benzene-heptane to yield 0.65 g (36%) of yellow crystals, mp 206° (sealed tube under N₂).

Anal. Calcd for C₄₃H₃₀F₅IrOP₂: C, 56.64; H, 3.32; F, 10.42; Ir, 21.08; O, 1.75; P, 6.79; mol wt 911. Found: C, 56.57; H, 3.33; F, 10.40; Ir, 21.5; O, 1.77; P, 7.04; mol wt 922 (cryoscopic in benzene).

Addition of Hydrogen Chloride to σ -Pentachlorophenylcarbonylbis(triphenylphosphine)iridium(I) (4). σ -Pentachlorophenylcarbonylbis(triphenylphosphine)iridium(I) (100 mg, 0.10 mmol) was dissolved in 5 ml of anhydrous benzene. Concentrated hydrochloric acid (5 ml) was added dropwise while the benzene solution was gently warmed. After 10 min the solution was cream colored. The solution was cooled and allowed to stir for 12 hr. The cream-colored crystals formed during this period were filtered, washed with hexane, and dried. Recrystallization from benzene-heptane under nitrogen yielded 93 mg (90%) of the addition product, mp 238° (open tube); mp 253° (sealed tube under N₂).

Anal. Calcd for C₄₃H₃₁Cl₆IrOP₂: C, 50.11; H, 3.03; Cl, 20.64; Ir, 18.65; O, 1.55; P, 6.01. Found: C, 50.56; H, 3.02; Cl, 20.44; Ir, 18.43; O, 1.50; P, 6.00.

Addition of Hydrogen Chloride to σ -Pentafluorophenylcarbonylbis(triphenylphosphine)iridium(I) (5). σ -Pentafluorophenylcarbonylbis(triphenylphosphine)iridium(I) (100 mg, 0.11 mol) was dissolved in 5 ml of anhydrous benzene. Concentrated hydrochloric acid (7 drops) was added and within 2 min the original yellow solution became colorless. The benzene solution was dried with anhydrous magnesium sulfate and filtered. Heptane (10 ml) was added and slow evaporation of the benzene-heptane solution afforded a white solid. Recrystallization of the solid from benzene-heptane yielded 103 mg (99%) of the addition product, mp 147° (sealed tube under N₂).

Anal. Calcd for C₄₃H₃₁ClF₅IrOP₂: C, 54.47; H, 3.30; Cl, 3.74; O, 1.69. Found: C, 54.67; H, 3.36; Cl, 3.29; O, 1.70.

When 15 mg of the addition product was heated in boiling ethanol for 10 min, the reaction mixture became yellow. Evaporation of the ethanol followed by drying of the yellow residue afforded 5, mp 205°.

Preparation of σ -Pentafluorophenyltris(diphenylmethylphosphine)iridium(I) (6). In a nitrogen-purged, 25-ml round-bottom flask equipped with a side-arm stopcock, σ -pentafluorophenylcarbonylbis(triphenylphosphine)iridium (200 mg, 0.22 mmol) and diphenylmethylphosphine (1.3 ml) were allowed to reflux in 10 ml of anhydrous benzene for 30 min. After cooling, the benzene was removed under reduced pressure to yield an oil. Heptane (10 ml) was added to this oil and produced a cloudy suspension which was heated to 80°. Sufficient methylene chloride was added to remove the cloudiness and the mixture was allowed to stand for 24 hr at -20°. The yellow-orange crystals which had formed were filtered. Recrystallization from methylene chloride-heptane produced 80 mg of σ -pentafluorophenyltris(diphenylmethylphosphine)iridium(I), mp 157°. The yield was 38%.

Anal. Calcd for C₄₂H₃₉P₃IrF₅: C, 56.30; H, 4.10; F, 9.90; Ir, 20.02; P, 9.68. Found: C, 56.17; H, 4.18; F, 9.88; Ir, 20.00; P, 9.79.

Acknowledgments. The authors are very grateful to Dr. Gary McVicker of the Esso Research & Engineering Co. for determining the molecular weight of 5 and to the National Science Foundation for a grant in support of this research program.

Registry No. IrCl(CO)(Ph₃P)₂, 15318-31-7; PhLi, 591-51-5; Ir(σ -C₆H₅)(CO)(Ph₃P)₂, 42402-07-3; C₆Cl₆MgCl, 31279-13-7; Ir(σ -C₆Cl₅)(CO)(Ph₃P)₂, 42402-08-4; C₆F₅MgBr, 879-05-0; Ir(σ -C₆F₅)(CO)(Ph₃P)₂, 42402-09-5; Ir(σ -C₆F₅)(Ph₂PMe)₃, 42402-10-8; HCl, 7647-01-0; Ir(H)(Cl)(σ -C₆Cl₅)(CO)(Ph₃P)₂, 42402-11-9; Ir(H)(Cl)(σ -C₆F₅)(CO)(Ph₃P)₂, 41021-67-4.

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