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## Facile Ortho Metalation of Triphenylphosphine in Five-Coordinated Methyliridium(III) Complexes

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**Abstract:** *trans*- $\text{IrCl}(\text{N}_2)[\text{P}(\text{C}_6\text{H}_5)_3]_2$  adds methyl sulfonates to give iridium(III)-dinitrogen complexes,  $\{\text{IrCl}(\text{O}_3\text{SY})(\text{CH}_3)(\text{N}_2)[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$  ( $\text{Y} = \text{CF}_3$  or  $\text{F}$ ). These react with anions in methanol to give five-coordinated iridium(III) complexes having the formula  $\{\text{IrClX}(\text{CH}_3)[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NCO}, \text{CH}_3\text{CO}_2, \text{NO}_3, \text{or NO}_2$ ). These form 1:1 adducts with carbon monoxide. The dichloro complex reacts with an excess of dimethylphenylphosphine to give *mer*- $\{\text{IrCl}_2(\text{CH}_3)[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_3\}$ . The coordinatively unsaturated methyl complexes ( $\text{X} = \text{Cl}, \text{Br}, \text{or NCO}$ ) undergo an ortho metalation of coordinated triphenylphosphine and eliminate methane. The process occurs in solution and in the solid state. In both cases the product is  $\{\text{IrC}_6\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\text{ClX}[\text{P}(\text{C}_6\text{H}_5)_3]_3\}$ . The kinetics of the reaction have been studied for  $\text{X} = \text{Cl}$  or  $\text{Br}$  in 1,2-dichloroethane. The observed first-order rate constants are, at 40 °C,  $(5.25 \pm 0.10) \times 10^{-4} \text{ s}^{-1}$  for  $\text{X} = \text{Cl}$  and  $(11.14 \pm 0.33) \times 10^{-4} \text{ s}^{-1}$  for  $\text{X} = \text{Br}$ . Deuteration of the ortho positions of the triphenylphosphines gives an isotope effect,  $k_{\text{H}}/k_{\text{D}}$ , of 1.51,  $\text{X} = \text{Cl}$ , and 1.21,  $\text{X} = \text{Br}$ . Activation parameters were obtained from the temperature dependence of  $k_{\text{obsd}}$ . Differential scanning calorimetry was used to measure the enthalpy change for the ortho-metalation reaction of  $\{\text{IrCl}_2\text{CH}_3[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$  in the solid state,  $\Delta H_0 = -2.6 \pm 0.1 \text{ kcal mol}^{-1}$ . The ortho-metalated product reacts with an excess of dimethylphenylphosphine to give  $\{\text{IrC}_6\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\text{Cl}[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_3\}\text{Cl}\cdot\text{CH}_3\text{OH}$ . The compounds have been characterized by IR, proton NMR, and electronic spectroscopy, elemental analyses, and molecular weight determinations.

Intramolecular substitution reactions by a metal on a coordinated ligand have attracted considerable interest because they represent the majority of examples of metal activation of carbon-hydrogen bonds in homogeneous solution. Recent reviews of the cyclometalation reaction have covered synthetic aspects and the very limited number of mechanistic studies.<sup>1-4</sup> Several examples of this type of reaction are found in tertiary phosphine and phosphite complexes of the platinum metals.<sup>3</sup> The majority involve a four-coordinate metal center with a  $d^8$  configuration where the ortho metalation can be accounted for as an intramolecular oxidative addition reaction.<sup>5</sup> Examples are known for rhodium(I), iridium(I), palladium(II), and platinum(II).<sup>3</sup> Bennett and Milner have reported some kinetic data for ortho metalation in chlorotris(triphenylphosphine)-iridium(I), but experimental difficulties prevented the determination of activation parameters.<sup>6</sup> This has been the only kinetic study of this type of reaction. Examples of the ortho metalation of phosphine and phosphite complexes of metals with  $d^6$  configurations are less common. The best studied examples are ruthenium(II) complexes of triphenylphosphine or triphenyl phosphite.<sup>7</sup> In ruthenium(II) systems the reaction has also been postulated to be part of the mechanism for catalytic hydrogenation of olefins using  $\text{RuHCl}(\text{PPh}_3)_3$ <sup>1</sup> and must be involved in the stoichiometric hydrogenation of active olefins by this compound.<sup>8</sup> A mechanism proceeding via an internal oxidative addition reaction of a five-coordinated complex has been proposed.

Few examples of ortho metalation in six-coordinated iridium(III) complexes have been studied. Ortho metalation in  $\text{IrHX}_2[\text{P}(\text{OC}_6\text{H}_5)_3]_3$  for  $\text{X} = \text{Cl}$  or  $\text{Br}$  apparently proceeds via a reductive elimination of  $\text{HX}$  to give  $\{\text{IrX}[\text{P}(\text{OC}_6\text{H}_5)_3]_3\}$  followed by an internal oxidative addition. For the iodo analogue a mixture of  $\text{H}_2$  and  $\text{HI}$  is eliminated (in boiling decalin) which might indicate that a pathway not involving prior generation of an iridium(I) species is possible.<sup>9</sup> Duff and Shaw have reported a study in which six-coordinated, dimethylnaphthylphosphine complexes of iridium(III) are ortho metalated under a variety of conditions. In general, high temperatures were required to bring about the reactions (e.g., refluxing in 2-methoxyethanol or fusing solid samples). In that paper, a 1,2-hydrometalation of coordinated ligand followed by  $\text{H}_2$  elimination was suggested to account for ortho metalation in a coordinatively saturated complex.<sup>10</sup> A mechanism involving the formation of coordinatively unsaturated species may be an alternative in light of the high temperatures used to bring about reaction. Coordinatively unsaturated species are ubiquitous intermediates in reactions in organometallic systems<sup>5</sup> and are often suggested as intermediates in  $d^6$  complex chemistry.

In this paper we report the synthesis and characterization of coordinatively unsaturated methyliridium(III) complexes which readily undergo ortho-metalation reactions under conditions which allow study of some of the important factors.

## Experimental Section

The compounds  $\{\text{IrCl}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$ ,<sup>11a</sup>  $\{\text{IrCl}(\text{N}_2)[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$ ,<sup>11b</sup>  $\{\text{RuCl}_2[\text{P}(\text{C}_6\text{H}_5)_3]_3\}$ ,<sup>12</sup>  $\{\text{RuHCl}[\text{P}(\text{C}_6\text{H}_5)_3]_3\}$ ,<sup>13</sup> and  $\text{P}(o\text{-D}_2\text{C}_6\text{H}_5)_3$ <sup>7</sup> were prepared by methods in the literature. Methyl trifluoromethanesulfonate (PCR), methyl fluorosulfonate (Aldrich), and trideuteriomethyl fluorosulfonate (Aldrich) were stored in vacuo in containers with Teflon stopcocks. Infrared spectra were recorded on a Perkin-Elmer 621 spectrometer, proton NMR spectra were obtained on a Varian T60 spectrometer using deuteriochloroform as solvent. Electronic spectra and kinetic data were obtained on a Cary 14. Molecular weights were determined on a Mechrolab 301A osmometer using chloroform as the solvent. Melting points were measured in open capillary tubes with a Mel Temp apparatus. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

$\{\text{IrCl}(\text{O}_3\text{SY})(\text{CH}_3)(\text{N}_2)[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$  ( $\text{Y} = \text{F}$  or  $\text{CF}_3$ ). Benzene, ca. 10–15 mL, and the appropriate methyl sulfonate, 0.3 mL, were condensed onto 1.0 g of  $\text{trans-}\{\text{IrCl}(\text{N}_2)[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$  at 77 K in vacuo. The mixture was allowed to warm to room temperature, then stirred until the yellow color of the dinitrogen complex had faded (about 15–20 min). The resulting white to cream colored solid was recovered and washed with benzene and ether and dried in vacuo. Yields are 0.9–1.0 g (80–90%).  $\text{Y} = \text{F}$ , mp 195–205 °C. Anal. ( $\text{C}_{37}\text{H}_{33}\text{ClIrN}_2\text{O}_3\text{P}_2\text{S}$ ) C, H, Cl, Y =  $\text{CF}_3$ , mp 153–155 °C. Anal. ( $\text{C}_{38}\text{H}_{33}\text{ClF}_3\text{IrN}_2\text{O}_3\text{P}_2\text{S}$ ) C, H, Cl, N.

$\{\text{IrClX}(\text{CH}_3)[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NO}_2, \text{NO}_3, \text{CH}_3\text{CO}_2$ , or  $\text{NCO}$ ). A solution of a salt of the appropriate anion (about 0.2–0.3 g) in methanol, 10 mL, was added to 1.0 g of the fluorosulfonato complex,  $\{\text{IrCl}(\text{O}_3\text{SF})(\text{CH}_3)(\text{N}_2)[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$ , and the resulting suspension was stirred. Conversion from cream color to the color of the new anion complex is accompanied by gas evolution. Reaction is complete within 15 min. In each case, except the cyanato complex, the product is insoluble in methanol and is recovered and washed with that solvent and water and dried in vacuo.

In the cyanato case, the product is soluble in methanol and is precipitated from the reaction mixture (a yellow solution) by addition of water. The resulting red solid is recrystallized from methylene chloride–*n*-hexane to give a violet solid.

The salts used, yields, and physical properties of the corresponding five-coordinated complexes are:  $(\text{CH}_3)_4\text{NCl}$  (90–95%), blue, mp 170–180 °C (solid changes to yellow in color). Anal. Calcd for  $\text{C}_{37}\text{H}_{33}\text{Cl}_2\text{IrP}_2$ : C, 55.35; H, 4.14; Cl, 8.83. Found: C, 54.87; H, 4.17; Cl, 8.65. Mol wt calcd 802, found 800.  $(\text{CH}_3)_4\text{NBr}$  (90–95%), green, mp 165–175 °C (solid changes to yellow in color). Anal. ( $\text{C}_{37}\text{H}_{33}\text{BrClIrP}_2$ ) C, H, Cl. Mol wt calcd 847, found 823.  $\text{KI}$  (90–95%), green, mp 180–195 °C (solid changes to yellow in color). Anal. Calcd for  $\text{C}_{38}\text{H}_{33}\text{ClIrP}_2$ : C, 49.70; H, 3.72; Cl, 3.96. Found: C, 47.64; H, 3.80; Cl, 3.10. Mol wt calcd 894, found 893.  $\text{KNO}_2$  (90–95%), orange, mp 184–185 °C. Anal. Calcd for  $\text{C}_{37}\text{H}_{33}\text{ClIrNO}_2\text{P}_2$ : C, 54.64; H, 4.09; N, 1.72. Found: C, 54.14; H, 4.13; N, 1.78. Mol wt calcd 813, found 768.  $\text{NH}_4\text{NO}_3$  (90–95%), yellow, mp 188–191 °C. Anal. ( $\text{C}_{37}\text{H}_{33}\text{ClIrNO}_3\text{P}_2$ ) C, H, N. Mol wt calcd 829, found 753.  $\text{NaO}_2\text{CCH}_3$  (90–95%), yellow, mp 190–191 °C. Anal. Calcd for  $\text{C}_{39}\text{H}_{36}\text{ClIrO}_2\text{P}_2$ : C, 56.69; H, 4.39; Cl, 4.29. Found: C, 56.47; H, 4.54; Cl, 4.88. Mol wt calcd 826, found 802.  $\text{KNCO}$  (50% after recrystallization), violet, mp 165–178 °C (solid changes to yellow in color). Anal. ( $\text{C}_{38.5}\text{H}_{34}\text{Cl}_2\text{IrNOP}_2$ ) C, H, N (compound contains 0.5 mol of  $\text{CH}_2\text{Cl}_2$ ). Mol wt calcd 852, found 817.

$\{\text{IrClX}(\text{CH}_3)(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NO}_2, \text{NO}_3, \text{O}_2\text{CCH}_3$ , or  $\text{NCO}$ ). A suspension or solution of 0.1 g of the appropriate five-coordinated complex in benzene (methylene chloride for the cyanato complex), 10 mL, was bubbled with carbon monoxide until it became colorless to light yellow in color. The iodo complex precipitated from the solution as it formed. In the remaining cases, the resulting solution was filtered and *n*-hexane added to the filtrate. Precipitation of the product occurred after cooling and scratching the flask with a stirring rod. The yield in each case was 0.07–0.08 g. The physical properties for the carbon monoxide adducts are as follows:  $\text{X} = \text{Cl}$ , light yellow, mp 205–206 °C. Anal. ( $\text{C}_{38}\text{H}_{33}\text{Cl}_2\text{IrOP}_2$ ) C, H, X =  $\text{Br}$ , yellow, mp 204–206 °C. Anal. ( $\text{C}_{41}\text{H}_{36}\text{BrClIrOP}_2$ ) C, H (compound contains 0.5 mol of  $\text{C}_6\text{H}_6$ ).  $\text{X} = \text{I}$ , orange, 205–207 °C. Anal. ( $\text{C}_{41}\text{H}_{36}\text{ClIrOP}_2$ ) C, H (compound contains 0.5 mol of  $\text{C}_6\text{H}_6$ ).  $\text{X} = \text{NO}_2$ , white, mp 203–206 °C. Anal. Calcd for  $\text{C}_{41}\text{H}_{36}\text{ClIrNO}_3\text{P}_2$  (includes 0.5 mol of  $\text{C}_6\text{H}_6$ ): C, 55.93; H, 4.12. Found: C, 55.45; H, 4.04.  $\text{X} = \text{NO}_3$ , white, mp 207–208 °C. Anal. Calcd for  $\text{C}_{41}\text{H}_{36}\text{ClIrNO}_3\text{P}_2$  (includes 0.5 mol of  $\text{C}_6\text{H}_6$ ): C, 54.94; H, 4.05. Found: C, 54.22; H, 4.30.  $\text{X} =$

$\text{O}_2\text{CCH}_3$ , white, mp 185–186 °C. Anal. Calcd for  $\text{C}_{43}\text{H}_{39}\text{ClIrO}_3\text{P}_2$  (includes 0.5 mol of  $\text{C}_6\text{H}_6$ ): C, 57.81; H, 4.40. Found: C, 57.10; H, 4.32.  $\text{X} = \text{NCO}$ , white, mp 215–221 °C. Anal. Calcd for  $\text{C}_{39.5}\text{H}_{34}\text{Cl}_2\text{IrNO}_2\text{P}_2$  (includes 0.5 mol of  $\text{CH}_2\text{Cl}_2$ ): C, 53.92; H, 3.89. Found: C, 54.56; H, 4.07.

*mer-}\{\text{IrCl}\_2(\text{CH}\_3)[\text{P}(\text{CH}\_3)\_2\text{C}\_6\text{H}\_5]\_3\}. A 0.2-g sample of  $\{\text{IrCl}_2(\text{CH}_3)[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$  and 0.1 mL of dimethylphenylphosphine was stirred for 5 min in 2 mL of benzene. The resulting yellow solution was evaporated to an oil, and ether was added. After standing 3 h at room temperature the solution was filtered to remove some cloudiness and the filtrate was refrigerated (–10 °C). The resulting yellow crystals were recovered and washed with ether, mp 200–210 °C. Yield 0.14 g. Anal. ( $\text{C}_{25}\text{H}_{36}\text{Cl}_2\text{IrP}_2$ ) C, H, Cl. NMR  $\text{CDCl}_3$ :  $\tau$  2.8 (m, 15, *P-C}\_6\text{H}\_5), 8.37 (t, 12, multiplet width = 8 Hz; two mutually trans  $\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5$  groups), 8.87 (d, 6,  $J_{\text{P-H}} = 8$  Hz,  $\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5$  trans to  $\text{CH}_3$ ), 9.08 (doublet of triplets, 3, *Ir-CH}\_3, cis  $J_{\text{P-Ir-CH}_3} = 3$  Hz, trans  $J_{\text{P-Ir-CH}_3} = 5.5$  Hz,  $\text{CH}_3$ ).***

$\{\text{IrC}_6\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\text{ClX}[\text{P}(\text{C}_6\text{H}_5)_3]\}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{or NCO}$ ). **Method A.** A 0.25-g sample of the appropriate methyl complex was heated to 180 °C, in vacuo, and held at that temperature for 20 min. The resulting yellow solid was recovered in quantitative yield.

**Method B.** A suspension of 0.2 g of methyl complex was refluxed for 24 h in toluene. The resulting yellow solid was recovered by filtration and washed with ether. Yield 0.16 g. Infrared spectra for samples prepared by the two methods were the same. The molecular weight of the ortho-metallated compounds is a function of concentration.  $\text{X} = \text{Cl}$ , mp 210 °C. Anal. ( $\text{C}_{36}\text{H}_{29}\text{Cl}_2\text{IrP}_2$ ) C, H, Cl. Mol wt, 1462 (15.1 g/L), 1420 (10.3 g/L), and 1139 (1.89 g/L).  $\text{X} = \text{Br}$ , mp 215 °C. Anal. ( $\text{C}_{36}\text{H}_{29}\text{BrClIrP}_2$ ) C, H, Cl; mol wt 1600 (15.0 g/L) and 1307 (3.45 g/L).  $\text{X} = \text{NCO}$ , mp 200 °C. Anal. ( $\text{C}_{37}\text{H}_{29}\text{ClIrNOP}_2$ ) C, H, Cl, N. Mol wt, 1073 (2.93 g/L).

Equilibrium constants for the monomer–dimer equilibrium were calculated from the molecular weight data. Values are  $(2 \pm 1) \times 10^3 \text{ M}^{-1}$  for the dichloro complex and  $(4 \pm 1) \times 10^3 \text{ M}^{-1}$  for the chloro-bromo compound.

**Methane Evolution from  $\{\text{IrClX}(\text{CH}_3)[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$ .** The solid compound, 0.3 g, was heated in vacuo to the temperature at which the ortho-metallation reaction occurred. The amount of gas was determined tensimetrically. Methane was identified by its vapor pressure at 77 K (found 10 Torr, lit. 10 Torr<sup>14</sup>) and by its infrared spectrum. Thermal decomposition of methyl complexes in which the ortho positions of the phenyl groups in triphenylphosphine were deuterated gave monodeuteriomethane. The results are summarized in Table III.

$\{\text{IrC}_6\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\text{Cl}[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_3\}\text{Cl}\cdot\text{CH}_3\text{OH}$ . A suspension of 0.3 g of  $\{\text{IrC}_6\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\text{Cl}_2[\text{P}(\text{C}_6\text{H}_5)_3]\}$  was stirred with 0.2 mL of dimethylphenylphosphine in benzene, 4 mL, under  $\text{N}_2$  for 20 min. The yellow mixture was filtered to remove cloudiness and 15 mL of methanol was added to the filtrate. Refrigeration (–20 °C) overnight resulted in formation of colorless crystals which were recovered and washed with cold methanol–ether (50–50), 2 mL. The filtrate was evaporated to an oil and 5 mL of methanol was added. Refrigeration caused further precipitation of product. Combined yield was 0.23 g of colorless crystals, mp 163–164 °C. The compound can be recrystallized from chloroform–methanol. NMR ( $\text{CDCl}_3$ ):  $\tau$  2.4 (m, 15.6,  $(\text{CH}_3)_2\text{PC}_6\text{H}_5$ ), 3.0 (m, 13.8,  $\text{P}(\text{C}_6\text{H}_5)_2\text{C}_6\text{H}_4$ ), 6.57 (s, 3,  $\text{CH}_3\text{OH}$ ), 8.10 (d, 6,  $J_{\text{P-H}} = 8$  Hz,  $\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5$  trans to ortho-metallated phenyl), 8.50 and 9.42 (two triplets, 6 protons each, multiplet width = 8 Hz, two mutually trans  $\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5$  groups). Anal. Calcd for  $\text{C}_{43}\text{H}_{51}\text{Cl}_2\text{IrOP}_4$ : C, 53.20; H, 5.30; Cl, 7.30. Found: C, 51.67; H, 4.92; Cl, 7.85.

**Synthesis of Complexes Containing Tri(*o*-deuteriophenyl)phosphine.** Triphenylphosphine deuterated in the ortho positions was prepared by the method of Parshall using  $\{\text{RuHCl}[\text{P}(\text{C}_6\text{H}_5)_3]_3\}$  as the catalyst.<sup>7</sup> The product was found by NMR and IR to be free of ortho protons. This was used to prepare  $\text{trans-}\{\text{IrCl}(\text{CO})[\text{P}(o\text{-D}_2\text{C}_6\text{H}_5)_3]_2\}$  by the standard methods. Other complexes were prepared from this by the same method used for the undeuterated complexes.

**Kinetic Data.** The course of reaction was followed spectrophotometrically with a Cary 14 spectrophotometer fitted with a water jacketed cell holder. The longest wavelength absorption band of the complexes was monitored. Plots of  $\ln(A - A_\infty)$  were linear for 5 half-lives at the lower temperatures. At the higher two temperatures the Guggenheim method<sup>15</sup> was used since a reproducible  $A_\infty$  could not be obtained. These data are given in Table IV. Rates were measured for samples continuously left in the light beam of the Cary 14

and for samples left out of the light beam except for absorbance readings. These were the same within experimental error.

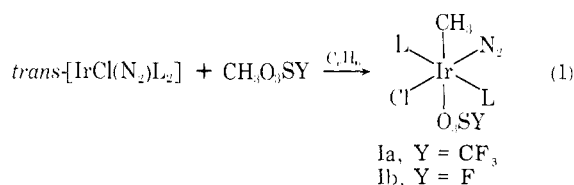
**Determination of  $\Delta H$  for the Conversion of  $[\text{IrCl}_2\text{CH}_3(\text{P}(\text{C}_6\text{H}_5)_3)_2]$  to  $[\text{Ir}(\text{C}_6\text{H}_5)_4\text{P}(\text{C}_6\text{H}_5)_2\text{Cl}_2][\text{P}(\text{C}_6\text{H}_5)_3]$  in the Solid State.** The technique used in differential scanning calorimetry was as previously described.<sup>16</sup> The accuracy of the technique was checked by measuring the heat of fusion of tin which was 1.69 kcal mol<sup>-1</sup> (lit. 1.69 kcal mol<sup>-1</sup>). This gave a value of  $\Delta H$  at the transition temperature (478 K) of 1.1  $\pm$  0.1 kcal mol<sup>-1</sup>, which was used to calculate  $\Delta H$  at 298 K from the following equation:<sup>17a</sup>

$$\Delta H_{298} = \Delta H_{478} - \int_{298}^{478} \Delta C_p dT$$

The contribution due to the heat capacities of the two iridium complexes was assumed to be negligible as was found in our previous work on similar complexes.<sup>17b</sup> Use of the heat capacity equation for methane in the above equation yields a value of  $\Delta H_{298} = -2.6 \pm 0.1$  kcal mol<sup>-1</sup>.

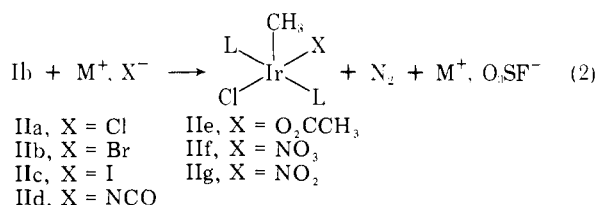
## Results

Six-coordinated methyliridium(III) complexes containing two readily replaceable ligands are obtained by addition of methyl sulfonates to *trans*- $[\text{IrCl}(\text{N}_2)\text{PPh}_3)_2]$ , eq 1. Compound



1a and its characterization have been previously reported by us in a communication.<sup>18</sup> The reactivity of the two compounds are the same so the availability of methyl fluorosulfonate favored the use of 1b in subsequent syntheses.

The utility of this iridium(III) dinitrogen complex in synthesis is illustrated by eq 2. Both the dinitrogen and fluoro-



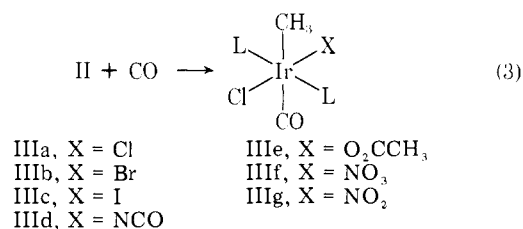
sulfonato group are labile in reactions with salts of coordinating anions. This allows the isolation of a series of complexes of formula  $[\text{IrClX}(\text{CH}_3)(\text{PPh}_3)_2]$ . Metathetical reactions of six-coordinated fluorosulfatoiridium(III) complexes have been described in the literature.<sup>19</sup> Molecular weight measurements establish that IIa-g are monomeric in chloroform. In compounds IIa-d the anion X cannot function as a bidentate ligand and these complexes therefore must be five-coordinated. They show absorption bands in the visible region of the spectrum (Table II) which is a good indicator of a coordinatively unsaturated iridium(III) species. The known series of penta-coordinate d<sup>6</sup> iridium complexes is colored while octahedral compounds are in general yellow to colorless.<sup>16,20,21</sup>

Infrared bands (Table I) assignable to the polyatomic acido ligands can readily be picked out in the spectra of compounds II d-g. The bands can reasonably be assigned by analogy with examples from the literature. In many of the complexes the methyl deformation mode  $\delta(\text{CH}_3)$  was evident in the range 1220-1240 cm<sup>-1</sup>.<sup>19</sup> In compound II d the cyanato ligand is probably N-bonded ( $\nu_a$  2245; 2191;  $\nu_s$  1344;  $\delta$  572),<sup>19,22</sup> but the assignment of linkage isomers of cyanate ion from IR data is not readily made.<sup>19,22,23</sup> The acetate ion in II e functions as a bidentate ligand ( $\nu_a$  1531 and  $\nu_s$  1416 cm<sup>-1</sup>) as it does in the analogous compound  $[\text{IrCl}(\text{H})(\text{O}_2\text{CCH}_3)(\text{PPh}_3)_2]$ .<sup>24</sup> The nitrate complex, II f, shows a number of IR bands<sup>22,23</sup> assignable to the nitrate ion. The separation of ca. 300 cm<sup>-1</sup> between the

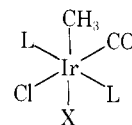
highest energy bands (1544 and 1518 cm<sup>-1</sup>) and the next highest (1260 and 1224 cm<sup>-1</sup>) is in the range observed for nitrate functioning as a symmetrical bidentate ligand,<sup>25</sup> but a mixture of linkage or geometric isomers in the solid cannot be ruled out. Complex II g shows a number of bands in the IR which must be due to the nitrite group. It appears that the isolated product is a mixture of nitro ( $\nu_a$  1405,  $\nu_s$  1310, and  $\delta$  820 cm<sup>-1</sup>) and nitrito isomers ( $\nu(\text{N}-\text{O})$  1125 and  $\delta$  820 cm<sup>-1</sup>) but no bidentate forms.<sup>22</sup> In these latter two cases, II f and g, the complexity of the spectra does not allow unambiguous assignment of structures. The dependence of  $\nu(\text{Ir}-\text{Cl})$  on X in the series of complexes is consistent with chlorine being trans to the added anion.<sup>26</sup> In the cyanato and nitrate complexes a band of unknown origin occurs at 351 cm<sup>-1</sup>.

The <sup>1</sup>H NMR spectra, Table I, of the compounds II d-f show a single triplet in the methyl region characteristic of a methyl cis to two triphenylphosphines. The nitrite complex II g shows a pair of triplets (ratio 2:1) which provides further support for the product being a mixture of isomers.

All of the complexes, II a-g, readily add carbon monoxide (eq 3). The infrared spectra of the compounds are consistent



with the anion X remaining trans to chlorine, the triphenylphosphines remaining trans,<sup>27</sup> and carbon monoxide adding trans to the methyl group. This is in accord with the growing list of cases in which nucleophilic addition to five-coordinated iridium(III) occurs trans to the ligand of highest trans influence.<sup>16,20,21,24</sup> These complexes are isomers of complexes prepared by Stroppe and Shriver by the addition of methyl fluorosulfate to Vaska's complex followed by substitution of anions, X, for the fluorosulfato group which gives the following product:<sup>19</sup>



Compounds III a-g show multiple bands in the  $\nu(\text{C}\equiv\text{O})$  region when samples are run as Nujol mulls but in solution spectra single bands are observed.

Due to the stoichiometry, the acetato and nitrate groups must function as monodentate ligands in III e and f, and the bands in the IR are in agreement with this assignment.<sup>23,25</sup> The cyanato ligand probably remains N-bonded though the  $\nu_a$  and  $\nu_s$  bands shift to higher frequencies.<sup>22</sup> The portion of the IR spectrum assignable to the NO<sub>2</sub> group is much simpler in compound III g than it is in II g and is consistent with coordination in the nitro form.<sup>22</sup> The isomer of this complex in which ion is trans to the methyl group exists as the nitrito complex.<sup>19</sup>

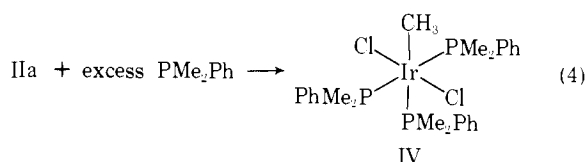
The <sup>1</sup>H NMR spectrum of III a, b, e, f, and g shows a triplet in the methyl region (ca.  $\tau$  8.68-9.08). There is a shift of about 1 ppm in going from the five-coordinated compounds II to the six-coordinated complexes reflecting a decreased electronegativity for the coordinatively saturated species.

Addition of an excess of dimethylphenylphosphine to complex II a yields *mer*- $[\text{IrCl}_2\text{CH}_3(\text{PMe}_2\text{Ph})_3]$ , IV (eq 4). This is characterized, in the IR, by a single  $\nu(\text{Ir}-\text{Cl})$  band at 308 cm<sup>-1</sup> consistent with mutually trans chloride ligands.<sup>28</sup> The NMR spectrum shows a doublet of triplets at  $\tau$  9.08 in the Ir-CH<sub>3</sub>

**Table I.** Infrared (cm<sup>-1</sup>, Nujol) and <sup>1</sup>H NMR Data (L = P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> and L' = P(CH<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>))

Complex	$\nu(\text{C}\equiv\text{O})$			Bands due to the anion X	$\delta(\text{CH}_3)$	Other	$\tau(\text{IrCH}_3)$	$J(\text{PIrCH}_3)$ (Hz)
	Nujol	1,2-C <sub>2</sub> -H <sub>4</sub> Cl <sub>2</sub>	$\nu(\text{Ir}-\text{Cl})$					
<b>IrClX(CH<sub>3</sub>)(N<sub>2</sub>)L<sub>2</sub></b> X = O <sub>3</sub> SCF <sub>3</sub>	—	—	320 (w)	1328 (s), 1230 (s), 1010 (vs)		$\nu(\text{N}\equiv\text{N})$ 2215 (s)	—	—
O <sub>3</sub> SF	—	—	328 (w)	1325 (s), 1209 (m), 1060 (m), 3510 (w), 580 (s)		$\nu(\text{N}\equiv\text{N})$ 2222 (w)	—	—
<b>IrClX(CH<sub>3</sub>)L<sub>2</sub></b> X = Cl	—	—	311 (m)	—	1230 (w), (940- CD <sub>3</sub> )		<i>a</i>	—
Br	—	—	308 (m)	—	1230 (m)		<i>a</i>	—
I	—	—	310 (vw)	—	1235 (m)		<i>a</i>	—
NO <sub>2</sub>	—	—	303 (w)	1405 (m), 1310 (m), 1245 (w)			7.52 <sup>c</sup>	6
				1125 (w), 820 (w), 814 (sh)	<i>b</i>		7.87 t	6
NO <sub>3</sub>	—	—	320 (w)	1544 (m), 1518 (m), 1260 (s), 1224 (s), 1064 (w), 930 (s)	<i>b</i>	351 (w)	7.88 t	6
O <sub>2</sub> CCH <sub>3</sub>	—	—	320 (w)	1531 (m), 1416 (sh)	1246 (vw)		8.00 t	6
NCO	—	—	312 (w)	2245 (s), 2192 (sh), 1344 (m), 586 (w), 572 (m)	1233 (w)	351 (m)	7.38 t	6
<b>IrClX(CH<sub>3</sub>)(CO)L<sub>2</sub></b> X = Cl	2030	2033	318 (m)	—	1224 (vw)		8.98 t	8
Br	2027	2031	313 (m)	—	1224 (vw)		8.95 t	8
I	2023	2013	300 (vw)	—			<i>a</i>	—
NO <sub>2</sub>	2050, 2036	2055 (br)	305 (w)	1400 (s), 1316 (s), 820 (s)	1223 (w)		<i>a</i>	—
NO <sub>3</sub>	2069, 2054, 2032	2059	323 (w)	1514 (s), 1263 (s), 965 (s)	1234 (sh)		8.77 t	7
O <sub>2</sub> CCH <sub>3</sub>	2055, 2038	2048	315 (w)	1631 (m), 1613 (m), 1356 (m), 1307 (m)			8.68 t	7.5
NCO	2059, 2032, 2018	2042	317 (w)	2272 (s), 2226 (sh), 1350 (m), 576 (m)	1225 (w)		9.08 t	7.5
<b>IrCl<sub>2</sub>(CH<sub>3</sub>)L'<sub>3</sub></b>	—	—	308 (m)	—			9.08 <sup>d,e</sup>	—
<b>IrC<sub>6</sub>H<sub>4</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>-CIXL</b> X = Cl	—	—	260–270 (vw)			1560 (m), 729 (m), 722 (s)	—	—
Br	—	—				1558 (m), 731 (sh), 729 (m), 723 (w)	—	—
NCO	—	—		2220 (s), 2165 (s)		1560 (m), 731 (m), 722 (w)	—	—
<b>[IrC<sub>6</sub>H<sub>4</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>-L'<sub>3</sub>Cl]<sup>+</sup>, Cl<sup>-</sup>-CH<sub>3</sub>OH</b>	—	—	283			3300 (br), 1635 (w)		

<sup>a</sup> Not sufficiently soluble to obtain an NMR spectrum, <sup>b</sup>  $\delta(\text{CH}_3)$  in region of bands due to the anion X, <sup>c</sup> Ratio 2:1, <sup>d</sup> The methyl resonance appears as a doublet of triplets;  $J(\text{PIrCH}_3)$ , 5.5 Hz (trans) and  $J(\text{P}_2\text{IrCH}_3) = 3.0$  Hz (cis). <sup>e</sup> NMR bands due to P(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub> are listed in the experimental section.



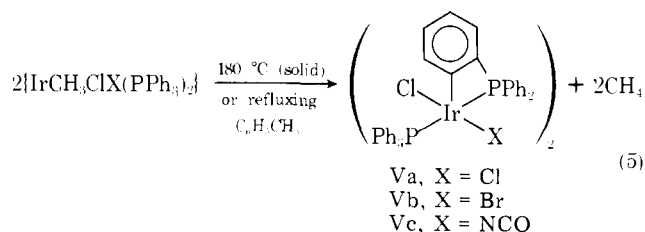
region assigned to a methyl trans to one phosphorus and cis to two equivalent phosphorus ligands. Confirmation of this geometry comes from the <sup>1</sup>H NMR of the P(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub> ligands. The methyl resonances appear as a doublet at  $\tau$  8.87 and a triplet at  $\tau$  8.37 in a ratio of 1:2. The doublet is due to the methyl groups on the phosphorus trans to the iridium bonded

methyl group and the triplet is due to the methyl groups on the mutually trans phosphorus atoms. The deceptively simple triplet is a consequence of the "virtual coupling" of the trans phosphorus atoms. The work of Shaw and Jenkins has established the use of the multiplicity of the methyl proton resonances of P(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub> in assigning geometries in a wide range of complexes of this ligand with the platinum metals.<sup>29</sup>

When solid samples of compound IIa are heated there is a color change from blue to yellow between 170 and 180 °C. This is accompanied by evolution of 1 equiv of gas, identified as methane by its IR spectrum and vapor pressure (eq 5). The

**Table II.** Electronic Spectra of  $\text{IrClX}(\text{CH}_3)[\text{P}(\text{C}_6\text{H}_5)_3]_2$  in 1,2-Dichloroethane

Complex	Wavelength at max, nm	Molar absorptivity ( $\text{M}^{-1} \text{cm}^{-1}$ )
X = Cl	555.0	489
	435.0	432
Br	575.0	648
	435.0	547
I	640.0	252
$\text{NO}_2$	460.0	269
$\text{NO}_3$	435.0	187
$\text{O}_2\text{CCH}_3$	430.0	178
NCO	360.0 (sh)	—
	540.0	791
	432.0	619



resulting yellow solid, Va, has new infrared bands at 1560, 735, and  $728 \text{ cm}^{-1}$  which are indicative of the ortho metalation of a phenyl group on triphenylphosphine.<sup>6,7,30</sup> Similar results are obtained for the bromo derivative, 11b, and the cyanato complex 11d. The compounds can be obtained by refluxing toluene suspensions of 11a and 11b, respectively. Molecular weights of Va, b, and c are concentration dependent in chloroform providing evidence for a monomer-dimer equilibrium in solution. Approximate values of the equilibrium constants calculated from the molecular weight data at  $39^\circ \text{C}$  are  $(2 \pm 1) \times 10^3 \text{ M}^{-1}$  for compound Va and  $(4 \pm 1) \times 10^3 \text{ M}^{-1}$  for compound Vb. The  $\nu(\text{Ir}-\text{Cl})$  region of the spectrum is featureless except for weak absorption in the  $270\text{--}280\text{-cm}^{-1}$  region. This may be assignable to a structure with  $\mu$ -chloro groups.<sup>31</sup>

The enthalpy change for reaction 5 in the solid state was determined by differential scanning calorimetry for the dichloro complex, 11a.  $\Delta H_0$  is  $-2.6 \pm 0.1 \text{ kcal mol}^{-1}$ .

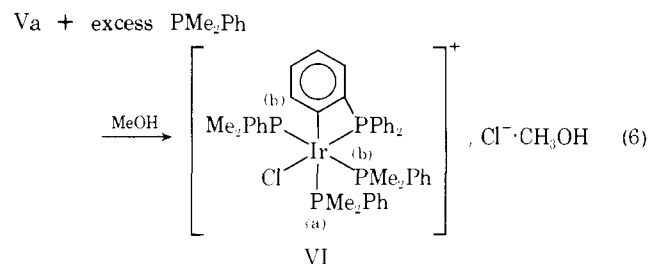
The remaining methyl complexes, 11d, e, f, and g, evolve 1 equiv of gas, identified as methane, upon heating solid samples to the decomposition point. In each case the remaining solid residue shows bands in the region of  $730 \text{ cm}^{-1}$ . These results are summarized in Table III. In solution the reactions of these compounds are complex, and we have not yet succeeded in isolating or identifying the products. The rate and probably the course of the reactions are markedly affected by sunlight. For example, the green color of solutions of the iodo complex, 11c, in benzene or 1,2-dichloroethane persists for days at room

**Table III.** Solid State Decomposition of  $\{\text{IrClX}(\text{CH}_3)[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$ 

X	Maximum Temp, $^\circ\text{C}$	Residue	Mol of $\text{CH}_4$ /mol of complex	IR bands of residue
Cl	178	Yellow solid	$1 \pm 0.05$	729, 722
Br	175	Yellow solid	1	732, 729, 722
I	192	Yellow solid	1	727, 721
$\text{NO}_2$	182	Decomposition	1	720
$\text{NO}_3$	188	Decomposition	1	717
$\text{O}_2\text{CCH}_3$	190	Decomposition	1	730, 720
NCO	175	Yellow solid	1	731, 722

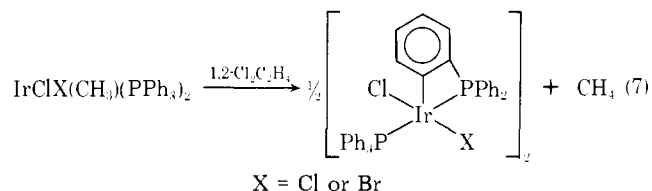
temperature in a foil wrapped flask but fades to yellow within 15 min when exposed to sunlight. Solid products from the reactions in light do not show the IR bands characteristic of the ortho metalated phenyl group.

Addition of an excess of dimethylphenylphosphine to the ortho-metalated complex Va in ether-methanol gives a cationic



derivative, VI (eq 6). The ortho-metalated triphenylphosphine group from Va is maintained; however, the chloride trans to the iridium-carbon bond is displaced. Such labilization has been observed in other iridium complexes.<sup>32</sup> The infrared spectrum of VI shows bands due to methanol and chloride trans to phosphorus,  $\nu(\text{Ir}-\text{Cl})$   $283 \text{ cm}^{-1}$ . The Jenkins-Shaw rules can again be used to establish the relative positions of the  $\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5$  ligands from the methyl resonance splitting patterns. The NMR spectrum shows two broad resonances in the phenyl region totaling 29 protons, a singlet at  $\tau$  6.57 (3 protons, methanol), a doublet at 8.10 (6 protons), and two triplets at 8.50 and 9.42 (6 protons each). The doublet can be assigned to the methyl groups on phosphorus (a) which is trans to the Ir-C bond. The two triplets indicate mutually trans phosphorus ligands and that there is no plane of symmetry in the molecule which includes the two phosphorus atoms (labeled b).<sup>29</sup> The geometry shown is consistent with these observations.

In homogeneous 1,2-dichloroethane solution the dichloro and chlorobromo complexes,  $\text{IrClX}(\text{CH}_3)(\text{PPh}_3)_2$  (11a, X = Cl and 11b, X = Br), cleanly react to give the ortho-metalated compounds Va and b, respectively. This was established by thin layer chromatography and by isolation of the complexes from this solvent. The rate of the reaction (eq 7) was followed using



spectrophotometric methods. Plots of  $\ln(A - A_\infty)$  vs. time were linear for five half-lives at the lower temperatures studied. Rate constants and activation parameters are listed in Tables IV and V. The effect of (1) added triphenylphosphine, (2) ortho deuteration of coordinated triphenylphosphine in 11a and b, and (3) deuteration of the methyl group on the rate of the ortho metalation were determined. The rate for the bromo complex was about twice that for the chloro complex. Addition

**Table IV.** Rate Constants for the Ortho Metalation of  $\{\text{IrClX}(\text{CH}_3)(\text{PPh}_3)_2\}$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ) and Deuterated Derivatives

Complex	Mol of added $\text{P}(\text{C}_6\text{H}_5)_3$ per mol of Complex	Temp, °C	$10^4k, \text{s}^{-1}$	
$\text{IrClX}(\text{CH}_3)[\text{P}(\text{C}_6\text{H}_5)_3]_2$ $\text{X} = \text{Cl}$	—	$40.0 \pm 0.1$	$5.25 \pm 0.10$	
	—	43.7	$7.31 \pm 0.06$	
	—	45.0	$8.39 \pm 0.10$	
	—	50.0	$13.65 \pm 0.03^a$	
	—	55.0	$21.11 \pm 0.10^a$	
	0.9	45.0	$6.47 \pm 0.09$	
	2.6	—	$6.20 \pm 0.10$	
	$\text{X} = \text{Br}$	—	30.0	$3.64 \pm 0.16$
		—	35.0	$5.45 \pm 0.14$
		—	40.0	$11.14 \pm 0.33^a$
—		45.0	$16.97 \pm 1.04^a$	
0.8		45.0	$14.01 \pm 0.37$	
1.5		—	$13.66 \pm 0.21$	
9.0	—	$11.98 \pm 0.20$		
$\text{IrClX}(\text{CH}_3)[\text{P}(o\text{-D}_2\text{C}_6\text{H}_3)_3]_2$ $\text{X} = \text{Cl}$	—	40.0	$3.35 \pm 0.10$	
	—	43.7	$4.87 \pm 0.12$	
	—	50.0	$8.93 \pm 0.10$	
	—	55.0	$14.50 \pm 0.13^a$	
	$\text{X} = \text{Br}$	—	45.0	$13.99 \pm 0.10$
		—	50.0	$13.36 \pm 0.93$
$\text{IrCl}_2(\text{CD}_3)[\text{P}(\text{C}_6\text{H}_5)_3]_2$	—	50.0	$8.57 \pm 1.20$	
$\text{IrCl}_2(\text{CD}_3)[\text{P}(o\text{-D}_2\text{C}_6\text{H}_3)_3]_2$	—	50.0	—	

<sup>a</sup> Calculated using the Guggenheim method.

**Table V.** Activation Parameters for the Ortho-Metalation Reaction of  $\{\text{IrClX}(\text{CH}_3)[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ )

Complex	$\Delta H^\ddagger$ , kcal mol <sup>-1</sup>	$\Delta S^\ddagger$ , eu
$\text{IrCl}_2\text{CH}_3[\text{P}(\text{C}_6\text{H}_5)_3]_2$	$+18.3 \pm 0.6$	$-15.2 \pm 2.0$
$\text{IrCl}_2(\text{CH}_3)[\text{P}(o\text{-D}_2\text{C}_6\text{H}_3)_3]_2$	$19.3 \pm 1.6$	$-13.1 \pm 5.0$
$\text{IrClBr}(\text{CH}_3)[\text{P}(\text{C}_6\text{H}_5)_3]_2$	$19.8 \pm 1.7$	$-9.0 \pm 5.4$

of triphenylphosphine to the reaction mixture produced a significant decrease in the rate of reaction for both complexes. The complete deuteration of the ortho position of the triphenylphosphine ligands in IIa and b revealed an isotope effect,  $k_{\text{H}}/k_{\text{D}} = 1.5 \pm 0.1$  (IIa) and 1.2 (IIb). Deuteration of the methyl group in IIa did not have a significant effect on the rate constant.

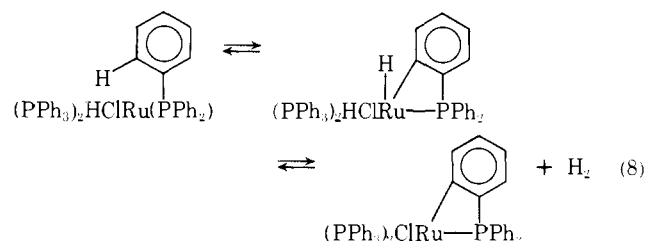
### Discussion

Five-coordinated complexes having a  $d^6$  configuration are most often encountered as reactive intermediates though examples of isolable compounds are known for ruthenium(II),<sup>7,12,13,33</sup> rhodium(III),<sup>34</sup> and iridium(III). The synthetic route starting with *trans*- $\{\text{IrCl}(\text{N}_2)(\text{PPh}_3)_2\}$  offers a unique opportunity for the rational synthesis of a homologous series of such compounds, and a number of examples of the type  $\{\text{IrRCIX}(\text{PPh}_3)_2\}$ <sup>19,20,21,35</sup> have been prepared. The isolable complexes allow some generalization to be made. Stability is favored by an R group having a high trans influence (e.g., H, C(O)R, S(O)<sub>2</sub>R, or CH<sub>3</sub>) and the absence of anions, X, which would be good bridging ligands and give dimers with coordinatively saturated metal sites. Anions which might act as chelating ligands may also give coordinatively saturated complexes. The importance of a ligand in the coordination sphere with a high trans influence is evident even in complexes where five coordination is also favored by sterically bulky ligands.<sup>36</sup>

No structures have been determined for compounds in the

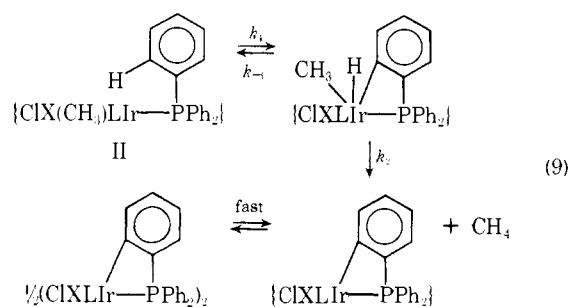
series of iridium complexes, but data obtained to date are consistent with a square pyramidal structure in which the group of highest trans influence, R, occupies the apex. Kinetic and synthetic study of the facile migration reactions of the coordinatively unsaturated acyl<sup>21,33</sup> and sulfonyl<sup>20</sup> derivatives have lent strong support to mechanisms for other reaction systems in which only indirect evidence or speculation led to the postulation of coordinatively unsaturated species.

In contrast to octahedral  $d^6$  complexes of phosphorus donor ligands which undergo ortho metalation only under forcing conditions,<sup>9,10</sup> the coordinatively unsaturated complexes  $\{\text{IrCH}_3\text{ClX}(\text{PPh}_3)_2\}$ ,  $\text{X} = \text{Cl}$  or  $\text{Br}$ , do so at a significant rate at room temperature in solution. This strongly suggests that in coordinatively saturated compounds the high temperatures required to bring about reaction may be necessary to cause dissociation of a ligand. This would be analogous to decarbonylation of the acyl group in  $\{\text{IrCl}_2(\text{CO})[\text{C}(\text{O})\text{CH}_3]_2(\text{PPh}_3)_2\}$ <sup>28</sup> at 145 °C compared to 0 °C for  $\{\text{IrCl}_2[\text{C}(\text{O})\text{CH}_3]_2(\text{PPh}_3)_2\}$ .<sup>28</sup> Stabilization of a coordinatively unsaturated intermediate might also account for the effect of sterically bulky phosphines in enhancing the ortho-metalation reaction.<sup>36</sup> No kinetic data have been reported for the ortho-metalation reaction of a  $d^6$ -metal complex, and mechanisms are based on the  $\{\text{RuHCl}(\text{PPh}_3)_3\}$  system which is the best characterized example. Evidence points to a five-coordinated species undergoing the oxidative addition-reductive elimination sequence shown in eq 8.<sup>1</sup>



The kinetic data for the reaction in eq 7 lend support to this type of mechanism. In the methyl complexes the minimum

sequence of steps is shown in eq 9 ( $L = PPh_3$ ).

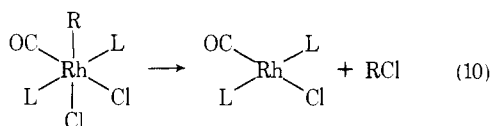


Loss of methane is not reversible and qualitative observations show the monomer-dimer equilibrium of the product, V, to be rapid compared to the disappearance of starting complex, II. If the seven-coordinate methyl-hydrido complex is assumed to have a low steady state concentration, the rate law for reaction 9 is:

$$-\frac{d[II]}{dt} = \frac{k_1 k_2 [II]}{k_2 + k_{-1}}$$

The first-order kinetic behavior of the reaction is consistent with two cases: (1) if the first equilibrium is rapid ( $k_{-1} \gg k_2$ ) then  $d[II]/dt = -K_{eq} k_2 [II] = -k_{obsd} [II]$  or (2) if  $k_2 > k_{-1}$  then  $d[II]/dt = -k_1 [II]$ . This would correspond to the reductive elimination of methane (case 1) or the oxidative addition (case 2) being the rate determining step. At present little kinetic data are available for these types of reactions in other systems. It is therefore worthwhile to discuss the kinetic parameters obtained in this work in more detail.

The isotope effects are small ( $k_H/k_D$  1.5 ( $X = Cl$ ) and 1.2 ( $X = Br$ )) and comparable to the value of 1.3 obtained by Bennett and Milner<sup>6</sup> for the internal oxidative addition reaction of  $\{IrCl(PPh_3)_3\}$ . No comparable data are available for a reductive elimination reaction. In both the insertion of the metal into an ortho carbon-hydrogen bond of a phenyl group and the elimination of a hydrocarbon molecule from the coordination sphere of a metal one would expect a small isotope effect if the bond forming or bond breaking processes were concerted.<sup>1</sup> There is also only limited data on the values of activation parameters for these two types of reaction steps. For intermolecular oxidative addition reactions of square planar iridium(I) complexes with organic halides, hydrogen, or dioxygen, a large negative activation entropy term ( $-20$  to  $-50$  eu) has been found to be a characteristic.<sup>37-39</sup> Stille and Regan<sup>40</sup> have reported kinetic data for the elimination reaction ( $L = PPh_3$ ) in eq 10 and report the following activation pa-



rameters:  $R = p\text{-ClC}_6\text{H}_4$ ,  $\Delta H^\ddagger = +25.9$  kcal mol<sup>-1</sup>,  $\Delta S^\ddagger = +9$  eu; and  $R = p\text{-ClC}_6\text{H}_4\text{CH}_2$ ,  $\Delta H^\ddagger = +20.5$  kcal mol<sup>-1</sup>,  $\Delta S^\ddagger = -3.6$  eu.

In the reaction sequence shown in eq 9 both steps ( $k_2$  and  $k_1$ ) would be expected to show a small deuterium isotope effect; therefore an assignment of rate controlling step cannot, at present, be made based on these data. The magnitude and negative sign of the activation entropies in Table V may tentatively be used as an argument against reductive elimination being the rate controlling step if one assumes that Stille's<sup>40</sup> values are representative of those for a reductive elimination process. The activation entropies obtained in this study are less negative than those for bimolecular oxidative addition reactions,<sup>37-39</sup> but a change in this direction would be expected for an intramolecular process. The slight decrease in rate caused

by added triphenylphosphine may reflect an inhibition of the oxidative addition step when the vacant coordination site in II is occupied. A more definitive analysis of the mechanism for this type of reaction will require more data from other systems so that reliable correlations may be formulated.

The enthalpy change measured for the ortho-metalation reaction of  $\{IrCl_2CH_3(PPh_3)_2\}$  in the solid state,  $\Delta H_0 = -2.6 \pm 0.1$  kcal mol<sup>-1</sup>, is probably a good approximation of the solution value<sup>16</sup> even though the dimerization of the ortho-metalated product complicates the interpretation of  $\Delta H_0$  by making an unknown contribution. One would anticipate a low  $\Delta H$  since the number of iridium-carbon and carbon-hydrogen bonds remains constant in the system.

The photosensitivity of some of the five-coordinated compounds suggests an area for further study. Photoreactions of many octahedral, d<sup>6</sup> complexes have been studied, and the generation of a five-coordinate complex has often been postulated to be the activation step.<sup>41</sup> The qualitative observations in this work suggest that the latter species might have significant photochemistry of their own in homogeneous solution.

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## Binding of Penicillamine to Toxic Metal Ions: Synthesis and Structure of Potassium (D-Penicillaminato)(L-penicillaminato)cobaltate(III) Dihydrate, $K[\text{Co}(\text{D-pen})(\text{L-pen})]\cdot 2\text{H}_2\text{O}$

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**Abstract:** The complex potassium (D-penicillaminato)(L-penicillaminato)cobaltate(III) dihydrate,  $K[\text{Co}(\text{D-pen})(\text{L-pen})]\cdot 2\text{H}_2\text{O}$ ,  $\text{C}_{10}\text{H}_{22}\text{CoKN}_2\text{O}_6\text{S}_2$ , has been synthesized and its crystal structure has been determined from three-dimensional single-crystal x-ray counter data. The complex crystallizes in the triclinic space group  $P\bar{1}$  with two formula units in a cell of dimensions  $a = 10.667$  (4) Å,  $b = 15.413$  (7) Å,  $c = 5.721$  (3) Å,  $\alpha = 106.64$  (3)°,  $\beta = 100.74$  (3)°, and  $\gamma = 64.88$  (2)°. Full-matrix least-squares refinement of the structure has converged to a  $R$  factor (on  $F$ ) of 0.038 for 2901 independent intensities. The geometry about the cobalt(III) centers is roughly octahedral, the ligating atoms being the S, N, and O atoms of the two penicillamine dianions. The isomer isolated is the all-cis isomer. The two Co-S bond lengths of 2.222 (2) and 2.229 (1) Å are similar to each other and to those in related complexes, but the Co-N distances of 1.922 (3) and 1.983 (3) Å and the Co-O lengths of 1.971 (2) and 1.942 (2) Å show a wide variation.

The increase in the industrial<sup>1</sup> and agricultural<sup>2</sup> use of metal and organometallic complexes of the last 2 decades has been accompanied by an increasing number of outbreaks of metal poisoning.<sup>1-3</sup> It is well established that toxic metal ions can, in some cases, be removed from the living system by the administration of chelating agents, which preferentially bind to the metal ions and, thereby, release them from the macromolecules (notably proteins) to which they coordinate. Many of the more successful chelating agents contain soft donors; thus, for example, dimercaptosuccinic acid,<sup>4</sup> BAL (2,3-dimercaptopropanol), and D-penicillamine ( $\beta,\beta$ -dimethyl-D-cysteine) contain sulfur atoms, and recent research<sup>5</sup> has suggested that selenium donors may be equally effective. Of the sulfur-containing chelating agents, D-penicillamine is the simplest to use since (unlike BAL), it is not toxic and can be administered in aqueous solution.

While the majority of chemical and clinical research has centered on the metals lead,<sup>6</sup> mercury,<sup>7</sup> and copper,<sup>8</sup> other metals are now commonly found in the environment; specifically, cobalt is in widespread industrial use<sup>9</sup> in catalytic processes, high-fidelity equipment, and pigments. The toxic effects of cobalt poisoning include heart disease and excess formation of red corpuscles; in the last decade, at least 40 people are known to have died from heart disease as a direct result of cobalt poisoning.<sup>10</sup> We have, therefore, initiated a study of the chelation of cobalt ions by therapeutic ligands.

The simplest complexes of transition metal ions with the potentially tridentate ligands cysteine, penicillamine, methionine, and their derivatives which would be anticipated are the *pseudo*-octahedral  $\text{ML}_2$  species; there is, however, no firm structural evidence for the existence of octahedral complexes  $\text{M}(\text{pen})_2$ , although recent work in our laboratories has established that this mode of binding does occur<sup>11</sup> for *S*-methyl-L-cysteine (SMC) anion in  $[\text{Co}(\text{SMC})_2]^+$  and for L-cysteine dianion (L-cys) in<sup>12</sup>  $[\text{Cr}(\text{L-cys})_2]^-$ .

We have, therefore, examined the reaction of cobalt(II) salts

with penicillamine, and here report the synthesis and crystal structure of the complex potassium (D-penicillaminato)(L-penicillaminato)cobaltate(III) dihydrate,  $K[\text{Co}(\text{D-pen})(\text{L-pen})]\cdot 2\text{H}_2\text{O}$ .

### Experimental Section

**Synthesis.** Cobalt(II) nitrate (0.005 mol in 7 mL of water) was added to D,L-penicillamine (0.015 mol in 20 mL of water) and the resulting mixture was stirred for a few minutes. Potassium hydroxide was added until the pH of the solution reached approximately 7. The solution was filtered and the filtrate allowed to stand; large olive green needles precipitated after several days. The crystals decompose slowly in air, with apparent loss of water, but their approximate composition was determined by chemical analysis and shown to be consistent with their formulation as a hydrate of  $K[\text{Co}(\text{D-pen})(\text{L-pen})]$ . The crystallographic experiments (vide infra) demonstrate that the original crystals are the dihydrate. Anal. Calcd for  $\text{C}_{10}\text{H}_{22}\text{CoKN}_2\text{O}_6\text{S}_2$ : C, 28.03; H, 5.18; N, 6.54; K, 9.13; S, 14.97. Obsd: C, 30.98; H, 5.03; N, 6.81; K, 9.86; S, 15.29.

**Collection and Reduction of the X-ray Data.** On the basis of Weissenberg and precession photography, the crystals were assigned to the triclinic system; the space group was initially selected as the centrosymmetric choice  $P\bar{1}$  ( $C_1^1$ ), and this was confirmed by the successful refinement of the structure (vide infra). The cell constants, obtained by least-squares methods,<sup>13</sup> are  $a = 10.667$  (4) Å,  $b = 15.413$  (7) Å,  $c = 5.721$  (3) Å,  $\alpha = 106.64$  (3)°,  $\beta = 100.74$  (3)°, and  $\gamma = 64.88$  (2)°. The observations were made at 21° with the wavelength assumed as  $\lambda(\text{Mo K}\alpha_1)$  0.7093 Å. A density of 1.749 g cm<sup>-3</sup> calculated for two molecules per cell is in acceptable agreement with the value of 1.76 (3) g cm<sup>-3</sup> observed by flotation. Hence, in space group  $P\bar{1}$ , no crystallographic symmetry is imposed on the molecules.

Intensity data were gathered from a prismatic crystal bounded by the (010), (0 $\bar{1}$ 0), (210), ( $\bar{2}$ 10), (00 $\bar{1}$ ), and (001) faces. The distances between these opposite pairs of faces were approximately 0.008, 0.016, and 0.064 cm, respectively. The crystal was mounted on a fiber roughly parallel to the  $a$  axis. The data were collected at a takeoff angle of 1.6°, with a receiving aperture 5.0 × 5.0 mm, placed 32 cm from the crystal. The data were collected by the  $\theta/2\theta$  scan technique, the scans being from 0.9° below the calculated  $\text{K}\alpha_1$  peak position to 0.9° above the