

INTERACTION OF THE LEWIS ACID HSO_3F WITH THE COMPOUND $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ AND THE SYNTHESIS OF TRANSITION METAL HYDRIDE COMPLEXES

G. GARZÓN *

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SUMMARY: The interaction of the Lewis acid HSO_3F with the transition metal base $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ has been studied. A new reaction in which an open coordination site remains after protonation has been developed. A convenient route to new compounds with cannot be prepared by direct oxidative addition reaction has been established.

UNITERMS: Transition Metal Hydride Complexes; Lewis Acid Compound $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$.

INTRODUCTION

The main reason for this study is the systematic investigation of HSO_3F as Lewis acid toward the transition metal base $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ and, second, the synthesis of novel cationic metal complexes.

Metal cations are usually regarded as acids. However there are many complexes of metals in low oxidation states where the metals serve as donors to one or more ligands^(1,2,3). The synthesis of new low oxidation state complexes has lead to new metal bases.

Substitution Reactions of $\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{H})(\text{SO}_3\text{F})$ with Various Anions.

In the study of the Lewis acid interactions of $\text{CH}_3\text{SO}_3\text{F}$ and $\text{CH}_3\text{SO}_3\text{CF}_3$ with Transition Metal bases⁽⁴⁾, it has been observed that in many cases reactions of the methyl carbenium ions closely paralleled protonation reactions. It was chosen $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ as the basic metal complex reactant.

Fluorosulfuric acid is one of the strongest of the simple protonic acids⁽⁵⁾. It has proved to be a very useful solvent for studying the protonation of very weak bases⁽⁶⁾. Addition of HSO_3F to $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ produces the highly labile oxidative addition product, $\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{H})(\text{SO}_3\text{F})$. The ready loss of SO_3F suggests that this complex would provide a convenient route to new

* Professor Assistente Doutor junto ao Departamento de Química da Universidade Del Valle — Cali — Colômbia.

compounds which cannot be prepared by direct oxidative addition reaction⁽¹⁾.



For example, addition of hydrogen halides (HX) to $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ gives an octahedral cis-addition product (i.e., H and X cis)⁽⁷⁾.



Reactions such as (2) yield metal hydride complexes which are not susceptible to substitution under mild conditions. For synthetic purposes it would be highly desirable to develop reactions in which an open coordination site remains after protonation. Hydrogen halides do not, in general, achieve this purpose because the halide ion is strongly held to the metal center.

EXPERIMENTAL SECTION

The HSO_3F and reagents were handled by standard Schlenk and syringe inert atmosphere techniques⁽⁸⁾ or were manipulated on a high vacuum line. Some of the solid samples were handled in a vacuum atmosphere, glove box or a glove bag purged with nitrogen. Analyses on air-sensitive samples were obtained from Schwarzkopf Microanalytical Laboratory, Woodside, New York. All solvents were distilled from appropriate dehydrating agents and were stored over Linde 4A molecular sieves under an atmosphere of nitrogen. HSO_3F was purified by trap-to-trap distillation. $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ was prepared and

purified according to published procedures⁽⁹⁾. Infrared Spectra were determined on Beckman Ir-9 or AR-12 spectrometers which were calibrated against polystyrene or water vapor. Spectra of solid samples were taken from Nujol or Fluorolube mulls between KBr plates or polyethylene sheets. In some cases a bean condenser was used working with very small samples. Medium infrared solution studies were conducted in CH_3NO_2 or CH_2Cl_2 using liquid cells with 1 mm spacing between NaCl windows. A varian T-60 (60 MHz) instrument was used to record the ^1H nmr spectra which were obtained from deuterated solvents.

SAMPLE PREPARATIONS

$\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{H})(\text{SO}_3\text{F})$. To 0.309 mmol of $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ in 40 ml of dry, air-free benzene was added 0.55 ml (0.309 mmol) of HSO_3F (0.58M in CH_3NO_2). The solution was vigorously stirred until the color dissipated (1 hour) and was then concentrated to about one third of the original volume by removal of the solvent under vacuum. Addition of 15 ml of dry, air-free heptane resulted in precipitation of the white solid $\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{H})(\text{SO}_3\text{F})$. Filtration of this product under N_2 , followed by washing with four 5 ml portions of hexane and drying under vacuum, yielded the air and moisture sensitive solid which could then be recrystallized from CH_2Cl_2 -heptane. The nature of this product was determined by medium and far infrared spectroscopy and elemental analysis.

Anal. Calcd for $\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{H})(\text{SO}_3\text{F})$: C, 50.49; H, 3.52; S, 3.63; P, 7.03; Cl, 4.02; Found: C, 51.10; H, 3.80; S, 3.91; P, 6.82; Cl, 4.25.

$\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{H})(\text{Cl})$. The preparation of this complex was: A 80 mg sample of $\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{H})(\text{SO}_3\text{F})$

was dissolved in 10 ml of CH_3NO_2 to give a pale yellow solution. A 20% excess of tetrabutylammonium chloride dissolved in CH_3NO_2 was then added to the stirred parent solution. After 30 minutes the white precipitate was filtered from solution and washed with several 5 ml portions of cold ether. The complex was then recrystallized from CH_2Cl_2 -hexane and dried under vacuum.

Anal. Calcd for $\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{H})(\text{Cl})$: C, 4.53; H, 3.79; Cl, 8.68; P, 7.58; Found: C, 4.65; H, 4.10; Cl, 8.95; P, 7.81.

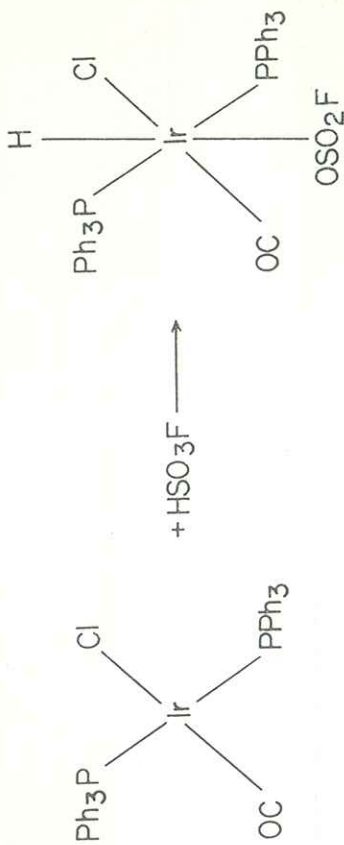
$\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{H})(\text{Y})$. When $\text{Y} = \text{Br}$, NCS the preparation was analogous to the above. The (methyl)-triphenylphosphonium bromide salt was dissolved in CH_3NO_2 . However, NH_4SCN was added as H_2O solution instead of CH_3NO_2 solution.

Anal. Calcd for $\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{H})(\text{NCS})$: C, 54.39; H, 3.69; Cl, 4.22; N, 1.66; Found: C, 55.30; H, 3.91; Cl, 4.16; N, 3.11.

RESULTS AND DISCUSSIONS

a) A solution of Vaska Compound reacts with HSO_3F in the ratio 1:1 to give the white solid $\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{H})(\text{SO}_3\text{F})$. This solid shows a high CO stretch (2058 cm^{-1} , Nujol Mull) which is evidence of electrophilic attack on the central metal atom (parent CO band is at 1956 cm^{-1}) indicating a six-coordinate oxidative addition product⁽³⁾.

stretches at 1340 and 1226 cm^{-1} . This indicates the anion is bound to the metal. In the polar solvent, nitromethane, this compound exhibits a pale yellow color due to dissociation into ions presumably because of the weak coordinating ability of the ligand. Dissociation of this group then leaves a cationic metal hydride complex which might be expected to



Infrared spectra of Nujol Mull of the SO_3F containing compounds show SO stretches characteristic of the coordinated group. The SO_3F complex showed SO react easily with more strongly coordinating anions. In the far infrared a band at 306 cm^{-1} is observed assignable as Ir-Cl stretch indicating⁽¹⁰⁾ that the Cl is trans to CO. In the medium infrared it

was observed at 2100 cm^{-1} a weak band even at highly concentrated mulls which can be assigned as Ir-H stretch.

b) The $\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{H})(\text{Cl})$ complex shows $\nu(\text{CO})$ at 2025 cm^{-1} (Nujol); $\nu(\text{Ir-Cl})$ at 315 cm^{-1} due to the Cl trans to CO and at 266 cm^{-1} due to the Cl trans to the H.

c) The $\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{H})(\text{Br})$ complex shows $\nu(\text{CO})$ at 2021 cm^{-1} ; $\nu(\text{Ir-H})$ at 2230 cm^{-1} .

d) The $\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{H})(\text{NCS})$ complex shows $\nu(\text{CO})$ at 2063 cm^{-1} ; $\nu(\text{CN})$ at 2103 cm^{-1} ; $\nu(\text{Ir-H})$ at 2187 cm^{-1} and $\nu(\text{IrCl})$ at 308 cm^{-1} .

The NCS group appears to be coordinated through the "hard" N atom⁽¹¹⁾. In CDCl_3 solution the ^1H nmr exhibits a triplet for the hydride group ($J = 22.66 \text{ Hz}$, $J_{\text{F-H}} = 12 \text{ Hz}$). The band at 308 cm^{-1} indicates that the chlorine is trans to CO therefore, H should be trans to the NCS group. However, the elemental analysis shows a nitrogen content twice the calculated value, indicating the possibility of having the group NCS coordinated to two sites. Further study of this reaction will be pursued in anhydrous conditions.

e) The reaction of $\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{H})(\text{SO}_3\text{F})$ with aqueous solution of NaNO_2 , KN_3 and NaCNO resulted in decomposition reactions or oxidation under the above conditions. For example, with an aqueous solution of NaNO_2 resulted in a yellow intractable product.

In conclusion reactions analogous to⁽¹⁾ should provide a synthetic route to a variety of transition metal hydride complexes. The reason for this is the high lability of the metal $-\text{OSO}_2\text{F}$ linkage.

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RESUMO: Estudou-se a interação do ácido de Lewis HSO_3F com $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$. Desenvolveu-se uma nova reação na qual, após protonação, permanece uma posição de coordenação livre. Estabeleceu-se uma nova maneira de obtenção de compostos que não podem ser obtidos por adição oxidativa direta.

UNITERMOS: Complexos de hidreto de metal e de transição; ácido Lewis, composto $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$.

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