Contribution from the Department of Chemistry
Northwestern University, Evanston, Illinois 60201, U.S.A.

The Lewis Basicity of Metal Complexes. BF_3 and $(C_6F_5)_3$ Adducts of $IrClCO(P(C_6H_5)_3)_2$ and Related Systems

R. N. Scott,[1a] **D. F. Shriver,**[1b] **and D. D. Lehman**[1c]

Received August 30, 1969

Tensimetric and spectrophotometric titrations demonstrate 1:1 and 2:1 interactions between BF_3 *and* $IrClCO(P(C_6H_5)_3)_2$, *while* BF_3 *only reacts in a 1:1 stoichiometry with* $IrClCO(P(C_2H_5)_2C_6H_5)_3$ *and* $IrClCO(PCH_3(C_6H_5)_2)_2$. *Similar adducts are formed when* $B(C_6F_5)_3$ *is employed in place of* BF_3. *Evidence is presented that the 1:1 adducts involve Ir to B donor-acceptor bonds. The relative affinities of some group III Lewis acids toward* Ir^I *bases are* $BF_3 > B(C_6F_5)_3 \gg B_2H_6$ *and* $Al_2(CH_3)_6 > Ga(CH_3)_3 \gg B(CH_3)_3$. *The classification of other ligands such as* O_2 *as Lewis acids is discussed.*

Introduction

Soon after his important discovery of molecular adducts of $IrClCO(P(C_6H_5)_3)_2$, **I**, with O_2, H_2 and other small molecules, Vaska found that BF_3-etherate interacts with **I**.[2]

Subsequently it was shown that **I** may add one or two moles of BF_3.[3] In the present paper further details are presented for BF_3 and a variety of other Lewis acids.

Experimental Section

All air-sensitive compounds were manipulated under nitrogen by Schlenk, syringe, or glove bag techniques; or in a chemical high-vacuum line.[3a] Spectrophotometric titrations in the near-uv were performed by incremental addition of Lewis acid to an evacuable cell[3b] containing a solution of the metal complex. Similarly, titrations were followed in the infrared by syringe sampling of reaction mixtures (in C_6D_6 solution) and injection of the sample into an IR tran 2 windowed cell. Tensimetric titrations were performed by a modification of standard procedures.[3c] Rapid equilibration was achieved by distilling BF_3 into the reaction vessel which was then sealed off (by means of a Teflon-in-glass needle valve). After shaking the reaction vessel for 4 minutes it was attached to the tensimeter, equilibrated at 5.5° and the pressure was recorded. Cryscopic titrations and molecular weights were determined in an air-tight apparatus equipped with a thermistor sensing element.[3d] The following spectrometers were employed: uv-Cary 14, ir-Beckman IR 9 or IR 12, ^{19}F nmr-Varian Hr 60 operating at 56.4 MHz, ^1H nmr-Varian A 60 and ^{11}B nmr-Bruker HFX-3 operating at 28.87 MHz. Accurate values for ^{19}F chemical shifts were obtained by the sideband technique coupled with repetitive determinations (each shift is an average of 8 scans). The chemical shifts measured in ppm from CF_3COOH external reference were extrapolated to the CCl_3F reference scale using $\delta(CCl_3F) = \delta(CF_3COOH) + 79.9$ ppm.

Purification and vapor pressure of the BF_3 have been described.[4] A sample of $^{10}BF_3$ (96% ^{10}B) was prepared by the pyrolysis of $CaF_2 . {}^{10}BF_3$ (Union Carbide Nuclear) and was fractionated through a trap at −131°; vp 65 mm at −126° (lit. 65).[5] Trimethyl boron was fractionated twice through a trap at −78° into one at −130° and the first fraction was discarded; vp 249.7 mm at −45.2° (lit. 245.7).[6] Preparation and purity of the trimethyl gallium sample is identical to that of a previous report.[7a] Trimethylaluminum was a commercial product (Ethyl Corp.) which was fractionated before use. Diborane was fractionated immediately prior to use, vp 69 mm at −126.6; lit 69 mm.[7b] A sample of $IrClCO(P(C_6H_5)_3)_2$ (I) was prepared by the method of Vaska and Diluzio[8] and confirmed by ir, and C and H analysis. A perdeuterated sample of **I** was prepared as described for **II** below. It displayed the expected infrared spectrum, and good analyses for C, D, Cl and P. Chlorocarbonyl-tris(p-biphenylphosphine)iridium(I), **II**, was prepared by a method which has been published for a variety of similar complexes.[9] The solid product was extracted under nirogen with toluene in a Soxhlet extractor. Crystals were obtained by concentrating the solution under vacuum. This yellow air-sensitive solid displays a CO stretch at 1956 cm^{-1}. *Anal.* Calcd.

---

[1] (a) National Institutes of Health Predoctoral Fellow 1966-1967. (b) Alfred P. Sloan Fellow. Addressee for correspondence. (c) NASA Trainee 1967-1968.

[2] L. Vaska, private communication.

[3] R. N. Scott, D. F. Shriver, and L. Vaska, *J. Amer. Chem. Soc.*, *90*, 1079 (1968).

[3] (a) D. F. Shriver, *The Manipulation of Air-Sensitive Compounds*, McGraw-Hill Book Co., New York, N. Y., 1969. (b) *ibid.*, p. 94-95. (c) *ibid.*, p. 61-63. (d) *ibid.*, p. 161-163.

[4] R. N. Scott and D. F. Shriver, *Inorg. Chem.*, *5*, 158 (1966).

[5] D. R. Stull, *Ind. Eng. Chem.*, *39*, 517 (1947).

[6] A. Stock and F. Zeidler, *Ber.*, *54*, 531 (1921).

[7] (a) D. F. Shriver and R. W. Parry, *Inorg. Chem.*, *1*, 835 (1962). (b) H. E. Wirth and E. D. Palmer, *J. Phys. Chem.*, *60*, 911 (1956).

[8] L. Vaska and J. W. Diluzio, *J. Amer. Chem. Soc.*, *83*, 2784 (1961).

[9] J. Chatt, N. P. Johnson and B. L. Shaw, *J. Chem. Soc.*, (A), 604 (1967).

for $C_{73}H_{54}ClIrOP_2$: C, 69.9; H, 4.40; Cl, 2.87; P, 5.01. Found: C, 69.8; H, 4.65; Cl, 3.13; P, 5.38. The sample of tris-p-biphenylphosphine used above was prepared by the reaction of PCl_3 with an ether solution of p-biphenyllithium (produced by a butyllithium-p-bromobiphenyl exchange). The total elemental analysis agreed with theory and the melting point, 177°, was in fair agreement with the literature, 172°.[10]

Chlorocarbonyl-bis(diethylphenylphosphine)iridium(I) was prepared as described previously.[9] Recrystallization from methanol-benzene produced golden yellow crystals which had good C and H analysis; mp 115-119; lit. 119-123°. Chlorocarbonyl-bis-(methyldiphenylphosphine)iridium(I) was prepared by the method of Sears[11] through a phosphine displacement on **I**. Identity of the product was confirmed by proton nmr, infrared, and C and H analysis.

Solvents used in the titrations and other physical measurements were purified as follows: Benzene and toluene were refluxed over CaH_2 and freshly distilled under N_2 (one sample of benzene was stored over Na-K alloy), deuterobenzene was dried over $LiAlH_4$, o-dichlorobenzene was dried over Linde Molecular Sieves 3-A, distilled under nitrogen and stored under nirogen over molecular sieves.

Results and Discussion

BF_3 Complexes. Two general stoichiometries of interaction were found: 2:1 for BF_3 with **I** or **II**, and 1:1 for BF_3 with all the iridium complexes (including compounds **I** an **II**). The limiting 2:1 stoichiometry of interaction is demonstrated by a rapid tensimetric titration, Figure 1. (Prolonged reaction times in the presence of excess BF_3 lead to slow additional BF_3 uptake and mixtures of products). This same stoichiometry is indicated by the treatment of **I** in *o*-dichlorobenzene with an excess of BF_3 followed by recovery and measurement of unreacted BF_3. The resulting ratio was 2.04:1. The 2:1 compound is stable under high vacuum and displays a 2063 cm^{-1} carbonyl bond. However treatment of the compound with Lewis bases like acetone or trimethyl amine regenerates the parent iridium complex.

In contrast to the 2:1 stoichiometry observed for the arylphosphine complexes, the arylalkylphosphine complex, $IrClCO(P(C_2H_5)_2C_6H_6)_2$, **III** and $IrClCO(PCH_3(C_6H_5)_2)_2$, **IV**, yield only 1:1 complexes. This is demonstrated by tensimetric titrations of **III** (Figure 1) and of **IV** (end-point 1.1 BF_3: 1.0 **IV**). Spectrophotometric titrations were carried out in an attempt to see if the arylphosphine complexes **I** and **II** might not add BF_3 in a stepwise fashion. The formation of a 1:1 complex with compound **I** is indicated by the disappearance of the CO stretching absorption of the parent complex at 1968 cm^{-1} and appearance of a new band at 2067 cm^{-1} (Figure 2). Interestingly, the ir titration also indicates no difference in CO stretching frequency between the 1:1 and 2:1 adducts. A similar but more accurate result

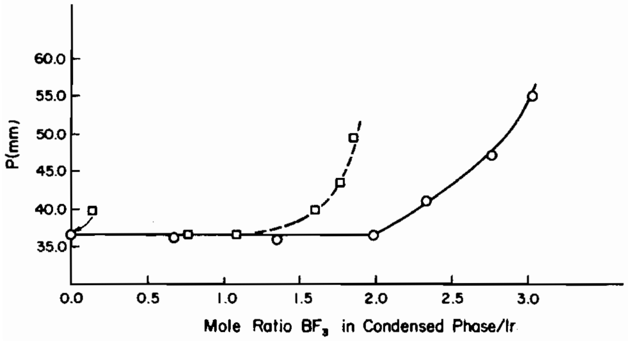

Figure 1. Tensimetric Titration with BF_3 in Benzene Solution at 5.5°. The verticle axis represents the total pressure (benzene plus boron trifluoride). The horizontal axis represents (net moles BF_3)/moles Ir complex; where (net moles BF_3)=(total moles BF_3)–(moles BF_3 in gas phase). ○ $IrCOCl(P(C_6H_5)_3)_2$; □ $IrCOCl(P(C_2H_5)_2C_6H_5)_2$.

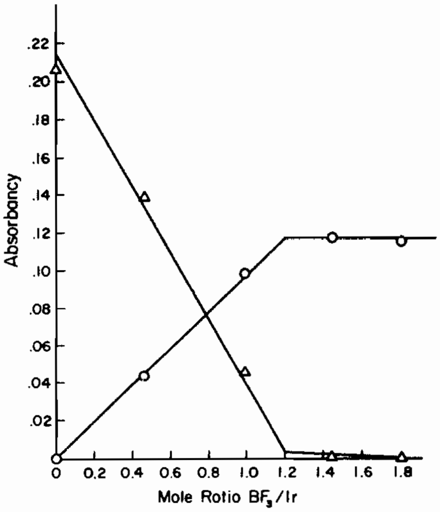

Figure 2. Infrared Titration of $IrCOCl(P(C_6H_5)_3)_2$ in C_6D_6 solution. △ 1968 cm^{-1}, (ν(CO) of parent complex; ○ 2067 cm^{-1}, ν(CO) of adduct.

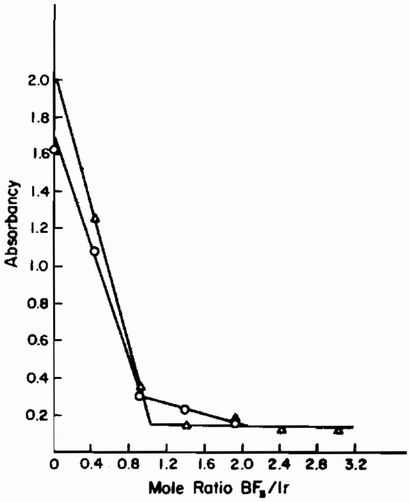

Figure 3. Spectrophotometric Titration of $IrCOCl(P(C_6H_5)_3)_2$. △ 387 nm band; ○ 338 nm band.

---

(10) D. E. Worrall, *J. Amer. Chem. Soc.*, *52*, 2933 (1930).
(11) C. T. Sears, Jr., Ph. D. Thesis, University of North Carolina, 1967.

Table I. Molecular Weight Data

Compound	Solvent	Nominal Molality [a] $\times 10^3$	Observed Molecular Weight	Formula Weight [b]
$IrCOCl(P(C_6H_5)_3)_2$	C_6H_6	5.10	701	780
$IrCOCl(P(C_6H_5)_3)_2$	C_6H_6	2.44	953	
$IrCOCl(P(C_6H_5)_3)_2$	$C_6H_4Cl_2$	5.32	780±54 [c]	
$IrCOCl(P(C_6H_5)_3)_2 . BF_3$	C_6H_6	4.56	1003	848
$IrCOCl(P(C_6H_5)_3)_2 . BF_3$	C_6H_6	2.28	793	
$IrCOCl(P(C_6H_5)_3)_2 . BF_3$	$C_6H_4Cl_2$	5.32	838±36 [c]	
$IrCOCl(P(C_6H_5)_3)_2 . 2BF_3$	C_6H_6	2.83	1160	916
$IrCOCl(P(C_6H_5)_3)_2 . 2BF_3$	C_6H_6	1.74	1057	
$IrCOCl(P(C_6H_5)_3)_2 . 2BF_3$	$C_6H_4Cl_2$	5.32	928±49 [c]	
$IrCOCl(P(C_2H_5)_2C_6H_5)_2$	C_6H_6	10.15	511	588
$IrCOCl(P(C_2H_5)_2C_6H_5)_2$	C_6H_6	6.31	526	
$IrCOCl(P(C_2H_5)_2(C_6H_5))_2 . BF_3$	C_6H_6	9.12	703	656
$IrCOCl(P(C_2H_5)_2(C_6H_5))_2 . BF_3$	C_6H_6	6.47	732	

[a] Based on formula weight of the parent compound. [b] Calculated for the formulas listed in Column 1. [c] These numbers re-present averages from 4 or 5 runs. The errors are the maximum deviations from averages.

Table II. Carbonyl Stretching Frequencies (in cm^{-1})

Compound	νCO
$IrCOCl(P(C_{12}H_9)_3)_2$	1956 [a]
$IrCOCl(P(C_{12}H_9)_3)_2 . 2BF_3$	2064 [a]
$IrCOCl(P(C_6H_5)_3)_2$	1968 [b]
$IrCOCl(P(C_6H_5)_3)_2 . BF_3$	2067 [b]
$IrCOCl(P(C_6H_5)_3)_2 . 2BF_3$	2067 [b]
$IrCOCl(P(C_2H_5)_2C_6H_5)_2$	1951 [b]
$IrCOCl(P(C_2H_5)_2C_6H_5)_2 . BF_3$	2055 [b]

[a] Nujol mull. [b] C_6D_6 solution.

was obtained when the titration was followed in the uv by the disappearance of bands at 387 and 338 nm (Figure 3). The formation of 1:1 adducts was also indicated by spectrophotometric (uv) titrations for compounds **II**, **III** and **IV**, (observed BF_3 to Ir ratios: 1.2:1, 1.0:1; and 1.1:1 respectively).

Even though the spectrophotometric titrations indicate 1:1 complexes in solution, it was not possible to isolate such complexes of **I** or **II**. In both cases solvent removal from a 1:1 mixture of BF_3 and Ir complex resulted in the appearance of two CO stretching frequencies in the solid (*e.g.* for **I** the solid product has bands at 1956 and 2063 cm^{-1}). No BF_3 was collected with the solvent. Thus it appears that for **I** and **II** the 1:1 complexes disproportionate to parent and 2:1 upon solvent removal. A possible driving force for this disproportionation is the much lower solubility of the 2:1 complex than the 1:1 complex.

The low solubility of Vaska's compound **I**, and its adducts, particularly the 2:1 complex, tends to complicate molecular weight measurements, but reasonably precise data were obtained for a variety of concentrations and two different solvents, (Table I). These results demonstrate that the parent complexes, their 1:1 adducts, and the 2:1 adducts are monomeric.

Infrared spectra for all of the boron trifluoride adducts (Table II) show an increase in the CO stretching frequency of *ca.* 100 cm^{-1} upon adduct formation. In addition, the IrCO deformation frequency appears to decrease from 606 in $IrCOCl(P(C_6H_5)_3)_2$ to 571 cm^{-1} in $IrCOCl(P(C_6H_5)_3)_2 . 2BF_3$ (Table III). These frequency shifts are in harmony with the proposition that boron is serving as an electron acceptor toward iridium which leads to decreased M–C bond order and increased C–O bond order. Comparison of far infrared spectra for $IrCOCl(P(C_6H_5)_3)_2$ and the related bromo-complex indicates that the Ir–Cl stretch occurs at 321 cm^{-1}. This band undergoes an increase of four wave numbers upon BF_3 addition (Table III). This very small increase indicates that BF_3 is not abstracting Cl or forming an Ir–Cl–B bridge, since the former should obliterate the 321 band and the latter should lead to a small decrease in the frequency.

The region of B–F stretching frequencies were studied in some detail. Three bands, not present in the spectrum of **I**, appear for the 2:1 adduct at 931, 960 and 1138 cm^{-1}. The 960 and 1138 absorptions increase in intensity and the 931 band decreases greatly when the adduct is prepared using $^{10}BF_3$. These results are consistent with the assignment of 960 and 931 bands to symmetric $^{10}BF_3$ and $^{11}BF_3$ stretching modes respectively. In this connection, bands at 939 and 952 cm^{-1} have been reported for the $^{11}BF_3$ and $^{10}BF_3$ symmetric stretching frequencies in $(CH_3)_3NBF_3$.[12]

Previous spectroscopic data suggest that the 1100 cm^{-1} region represents asymmetric BF_3 stretching.[11] To make this region accessible it was necessary to study the adducts of **I** and its perdeuterated analog. The results tabulated in Table III clearly show the expected isotope effects. The B–F frequencies for both symmetric and asymmetric stretching are surprisingly sharp. From these data it appears that the 2:1 adducts contain coordinated BF_3. Similarly the ^{11}B nmr of $IrCOCl(P(C_2H_5)_2C_6H_5) . BF_3$ in chloroform displayed a signal at +18.2 ppm from $B(OCH_3)_2$. This is in the correct region for BF_3 adducts.

B–F stretching frequencies for three-coordinated boron are expected in the 1300-1500 cm^{-1} region.[13] Accordingly, the 1160-1700 cm^{-1} region was investigated for perchlorobutadiene mulls of the 2:1 adduct of **I**, and these were compared to spectra obtained on Nujol mulls. The resulting composite spectrum along with the spectrum of $IrClCO(P(C_6D_5)_3)_2 . 2BF_3$ clearly indicates the absence of $-BF_2$ groups.

Since triphenylphosphine abstraction by BF_3 is one

---

(12) R. L. Amster and R. C. Taylor, *Spectrochim. Acta.*, *20*, 1487 (1964).

(13) D. F. Shriver, J. F. Jackovitz and M. J. Biallas, *Spetrochim. Acta*, *24A*, 1469 (1968), and references therein.

Table III. Infrared Spectra (Frequencies in cm^{-1})[a]

Compound	ν_{CO}	δ_{MCO}	ν_{Ir-Cl}	^{11}B–F $\nu_{asymmetric}$	^{10}B–F $\nu_{asymmetric}$	^{11}B–F $\nu_{symmetric}$	^{10}B–F $\nu_{symmetric}$
$IrCOCl(P(C_6H_5)_3)_2$	1956	606	321	—	—	—	—
$IrCOCl(P(C_6H_5)_3)_2 . 2BF_3$	2063	571	325	[b]	1138	931	960
$IrCOCl(P(C_6H_5)_3)_2 . 2B^{10}F_3$	2063	571	—	[b]	1139 m	931	961
$IrCOCl[P(C_6D_5)_3]_2$	1956	—	—	—	—	—	—
$IrCOCl[P(C_6D_5)_3] . 2BF_3$	2063	—	—	1104	1140	930	966

[a] Nujol mulls. [b] Masked by $P(C_6H_5)_3$ absorption.

possible mode of interaction, the spectrum of $F_3BP(C_6H_5)_3$ was determined on a mulled sample. In the asymmetric BF_3 stretching region a broad band was observed extending from 1100 to 1150 cm^{-1}; while the symmetric stretch region contains two bands at 915 and 888 cm^{-1} which have the correct positions and intensities for the ^{10}B and ^{11}B isotopic species respectively. The band shapes and particularly the symmetric stretching frequencies demonstrate that BF_3 has not abstracted triphenylphosphine in the formation of $IrClCO(P(C_6H_5)_3)_2 . 2BF_3$.

The foregoing data are consistent with the 1:1 adducts containing Ir–BF_3 bonds. A variety of geometries have been observed for the molecular adducts of Vaska's compound;[14] so it does not seem reasonable to speculate on the exact configuration of the 5-coordinated 1:1 BF_3 adduct.

The 2:1 adduct is structrally puzzling. Coordination of the second BF_3 to Cl appears to be ruled out by the far-infrared data. Coordination of both BF_3 molecules to Ir appears unlikely since the CO frequency does not shift on converting the 1:1 adduct to the 2:1. Finally, a third possibility is that the second BF_3 molecule is coordinated to the first by means of a B–F–B bridge. This would imply an induced basicity in the fluorines of the first BF_3 upon coordination to the iridium. There is considerable precedent for this phenomenon.[15-19] However, the resulting B_2F_6 adduct should have a hyghly unsymmetrical structure which should lead to a complex infrared spectrum in the B–F stretching region.[18] The simple pattern observed for the 1:2 adduct is inconsistent with such a structure and is indicative only of the existence of two apparently equivalent four-coordinate BF_3 groups.

Thus, any proposed structure must take account of the equivalence of the carbonyl stretching frequencies of the 1:1 and 1:2 adducts, the very small increase in the Ir–Cl stretching frequency upon formation of the 1:2 adduct, the presence of simple four-coordinate BF_3 groups, and the fact that the 1:2 adduct is monomeric in benzene. None of the structures proposed above fulfills all of these erquirements, and the structure of the 1:2 adduct thus remains an open question.

$B(C_6F_5)_3$ Complexes. This Lewis acid was employed because it is similar in acidity to BF_3 but afforded somewhat more soluble adducts. A spectrophotometric (379 and 335 nm) titration of $IrClCO(P(C_2H_5)_2C_6H_5)_2$ with $B(C_6F_5)_3$ in benzene solution demonstrates 1:1 interaction. A cryscopic titration in benzene also indicates a 1:1 adduct but additional affinity for the acid is indicated by the shallow slope between 1:1 and 2:1 stoichiometries and the steep slope thereafter (Figure 4). The CO stretching frequency for $IrCOCl(P(C_2H_5)_2C_6H_5)_2 . B(C_6F_5)_3$ in hexadeuterobenzene is 2046 which is only 9 cm^{-1} lower than the corresponding BF_3 adduct.

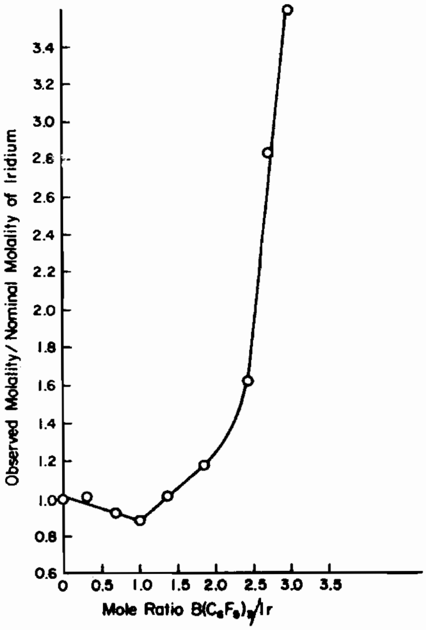

Figure 4. Cryscopic Titration of $IrCOCl(P(C_2H_5)_2C_6H_5)_2$ with $B(C_6F_5)_3$, in Benzene Solution.

In constrast, **I** and **II** appear to have only moderate affinities for $B(C_6F_5)_3$. For example a spectrophotometric titration of Vaska's compound produces a smooth curve which may be analyzed in terms of the following equilibrium:

$$IrClCO(PR_3)_2 + B(C_6F_5)_3 = IrClCO(PR_3)_2 . B(C_6F_5)_3$$

for which the eight points yield an equilibrium constant of $2.7 \pm 0.3 \times 10^3$ l/mole. Similarly, the titration curve for the tris(biphenyl)phosphine complex **II**

---

(14) S. J. LaPlaca and J. Ibers, *J. Amer. Chem. Soc., 87,* 2581 (1965). S. LaPlaca and J. A. Ibers, *Inorg. Chem., 5,* 405 (1966). J. S. McGinnety and J. A. Ibers, *Chem. Commun., 235,* (1968).

(15) H. C. Brown, P. F. Stehle, and P. A. Tierney, *J. Am. Chem. Soc., 79,* 2020 (1957).

(16) R. D. W. Kemmitt, R. H. Nuttall, and D. W. Sharp, *J. Chem. Soc.,* 46 (1960).

(17) J. J. Rupp and D. F. Shriver, *Inorg. Chem., 6,* 755 (1967).

(18) S. Brownstein and J. Paasivirta, *Can. J. Chem., 43,* 1645 (1965).

(19) J. J. Harris, *Inorg. Chem., 5,* 1627 (1966).

Table IV. ^{19}F Chemical Shifts of Some Pentafluorophenyl Derivatives ppm relative to CCl_3F

	Chemical Shifts				
Compound	ortho	para	meta		Reference
C_6F_5Br	132.54	154.65	160.60	Carbon tetrachloride	[a]
C_6F_5Br	135.31±.01	157.10±.02	162.73±.02	benzene	[b]
$B(C_6F_5)_3$	128.7	144.3	160.6	pentane	[c]
$B(C_6F_5)_3$	137.00±.04	157.18±.05	164.98±.05	benzene	[b]
$IrCOCl(PEt_2Ph)_2 . B(C_6F_5)_3$	137.03±.14	161.97±.04	166.83±.04	benzene	[b]
$B(C_6F_5)_4NEt_4$	131.2	163.5	167.1	acetone	[c]
$LiB(C_6F_5)_4$	131.6	164.2	167.9	ether	[c]
$B(C_6F_5)_3 . NH_3$	134.2	157.3	163.9	ether	[c]
$B(C_6F_5)_3py$	130.7	157.1	163.5	ether	[c]
$B(C_6F_5)_3NMe_3$	135.6	159.4	164.4	chloroform	[c]

[a] N. Boden, J. W. Emsley, J. Feeney and L. H. Sutcliffe, *Molec. Phys., 8,* 133 (1964); internal reference. [b] This work; external reference. [c] A. G. Massey and A. J. Park, *J. Organometal. Chem., 5,* 218 (1966); internal reference.

may be analyzed in terms of $K = 1.77 \pm 0.07 \times 10^3$ l/mole for six data points ranging from 0.4 to 2.8 mole ratio of acid to metal complex. Although $B(C_6F_5)_3$ has a much smaller affinity than BF_3 for the arylphosphine complexes, the CO stretching frequency of $IrClCO(P(C_6H_5)_3)_2 . B(C_6F_5)_3$ is 2061 in hexadeuterobenzene, which is only 6 cm^{-1} lower than that of the BF_3 complex. It is probable that at least part of the reduced affinity of tris(pentafluorophenyl)boron toward the iridium complexes is due to steric crowding.

The fluorine nmr spectrum was obtained for a benzene solution of $IrClCO(P(C_2H_5)_2C_6H_5)_2 . B(C_6F_5)$. A doublet centered at 137.0±0.1 ppm relative to CCl_3F, a triplet centered at 161.97±.04 and a triplet at 166.83±.04 are attributed to ortho, meta and para fluorines respectively. This represents a net shielding of the para fluorine of 5 ppm from the free acid (Table IV). While exact comparisons are difficult owing to the use of differing solvents, the results summarized in Table IV indicate that a shift of this magnitude is characteristic of $B(C_6F_5)_3$ adduct formation. Thus the tris(pentafluorophenyl)boron compounds like the boron trifluoride 1:1 compounds are straight forwardly interpreted as simple metal-boron donor-acceptor compounds.

$B(CH_3)_3$, $Al_2(CH_3)_6$, $Ga(CH_3)_3$ and B_2H_6 Systems. A tensimetric titration of compound **I** (6.25×10^{-3} *M* in benzene) with diborane produced a linear increase in pressure with increasing B_2H_6:**I** ratio. Thus, under the conditions of this experiment (5.5°C and B_2H_6 pressure less than 22 mm) there was no significant compound formation. Similar experiments in which compounds **I** and **III** were titrated with $B(CH_3)_3$ also indicated no adduct formation.

The Lewis acids $Al_2(CH_3)_6$ and $Ga(CH_3)_3$ exhibit rather complex behavior. Spectrophotometric titrations of **I** with $Al_2(CH_3)_6$ displayed a progressive decrease in the 387 and 338 nm bands of **I**. However the data do not appear to be amenable to analysis in terms of a simple equilibrium. It does appear that a simple adduct is being formed because of the characteristic decrease in the 387 and 338 nm bands and the appearance of a new CO stretching frequency at 1970 cm^{-1}. However after this solution stood for 24 hours the CO stretching region was clear, indicating an irreversible destruction of the complex. Another complication is the appearance of new visible-uv absorptions at 414, 373 and 351 nm at approximately a 2:1 $Al_2(CH_3)_6$ to **I** ratio (solution 5.34×10^{-4} m **I** and 11.07×10^{-4} m $Al_2(CH_3)_6$).

While the treatment of compound **I** with a very large excess of $Ga(CH_3)_3$ yields a red-orange solution or solid, it was not possible to isolate a stable complex. Similarly a tensimetric titration of **I** (2.4×10^{-4} m in benzene) with $Ga(CH_3)_3$ failed to show any interaction up to a 15-fold excess of the acid. With the more basic diethylphenylphosphine complex, III, a steady decrease in the 379 nm band was observed upon incremental addition of $Ga(CH_3)_3$. These data can be analyzed in terms of a formation constant of 1.2×10^3 $molal^{-1}$.

Classification of Lewis Acid Ligands. It has been pointed out that O_2, $C_2(CN)_4$ and SO_2 can form bonds to iridium in which two types of interactions occur.[20-23] These are (1) weak donation from filled π orbitals in O_2 and $C_2(CN)_4$ or nonbonded electron pairs in SO_2 and (2) acceptance of electron density from the metal by vacant orbitals on the ligand. However, in the case of the boron trifluoride adduct the only interaction is a donation from iridium to boron. Therefore, it is of interest to compare physical and chemical characteristics of the various molecular adducts with the BF_3 complex to clarify the relative importance of donor *vs* acceptor character of the ligands.

Previously, it was shown that there is a linear correlation between the CO stretching frequency of an adduct of Vaska's compound and the electron affinity of the added molecule.[3] The correlation holds well for the parent compound, and its adducts.[24] The correlation is of approximate significance only because the detailed geometry of the adduct may

---

(20) L. Vaska and S. S. Bath, *J. Am. Chem. Soc., 88,* 1333 (1966).

(21) J. A. McGinnety, R. J. Dodens and J. A. Ibers, *Science, 155,* 709 (1967).

(22) W. H. Baddley, *J. Am. Chem. Soc., 88,* 4545 (1966).

(23) J. A. McGinnety and J. A. Ibers, *Chem. Commun.,* 235 (1968).

(24) Recently an NO+ adduct of Vaska's compound was reported by D. J. Hodgson, and J. A. Ibers (*Inorg. Chem., 8,* 1282 (1969)), who show that the structure is most easily explained by invokin an Ir-toNO+ donor-acceptor bond. However, the electron affinity of NO+ contains an electrostatic contribution that is absent for the neutral acceptors and therefore $IrClCO(P(C_6H_5)_3)_2 . NO^+$ cannot be included in the correlation of ν(CO) with electron affinity.

affect the CO stretching frequency and electron affinities do not exactly parallel Lewis acidities. The implication from this correlation, which includes a simple σ Lewis acid-BF_3, is that the dominant type of interaction between Ir and any of the added molecules is metal-to-ligand donor-acceptor bonding. A number of other features are consistent with this view. Thus the O–O distance in the O_2 adduct is near that of O_2^{2-} and the geometry of the SO_2 adduct is most easily explained in terms of metal-to-SO_2 donor-acceptor bonding.[25]

In a broader sense, ligands such as H_2O and NH_3 are donors, those such as PF_3 and CO participate in both donor and acceptor interaction, and finally BF_3 is an example of an acceptor ligand. There are no sharp lines separating these three classes and the best classification for a ligand may vary with the electronic structure of the central atom. However, ligands such as $Ga(CH_3)_3$, BF_3, O_2, C_2F_4 and $C_2(CN)_4$, are on the acid side of the classification scheme because their dominant mode of bonding is electron acceptance. Also the greater affinity of $IrCOCl(P(C_2H_5)_2(C_6H_5))_2$ than $IrCOCl(P(C_6H_5)_3)_2$ for O_2 and for $Ga(CH_3)_3$ can be attributed to the greater basicity of the former iridium compound. In summary, the Lewis acid classification for certain ligands is helpful in systematizing their chemistry.

Relative Acidities Toward Ir(I). It is interesting to compare the affinities of various Lewis acids for metal complexes in order to understand the systematics of Lewis acid-base interaction for metals. For the boron-containing acids the relative order of acidity is $BF_3 > B(C_6F_5)_3 \gg B_2H_6, B(CH_3)_3$. Thus the BF_3 vapor pressure over the various iridium complexes is significantly less than 1 mm, while $B(C_6F_5)_3$ adducts of the Ir(I)-aryl phosphine complexes are extensively dissociated in solution. As discussed above this difference may be due to steric and/or electronic effects. Of more interest is the much greater affinity of these metal bases for BF_3 than B_2H_6, which is the same order as observed previously with bis-cyclopentadieyl metal hydrides as metal bases.[26] This relative affinity is analogous to the greater stability of metal trifluoromethyl complexes over the corresponding methyl complexes.

Although the aluminum and gallium alkyl systems are quite complex and not amenable to quantitative treatment it does appear that the relative affinities are $Al_2(CH_3)_6 > Ga(CH_3)_3 > B(CH_3)_3$. This trend in stability is identical to that found by Brunner, Waieles and Kaesz[27] for bis-cyclopentadieyl metal hydrides and by others for main group bases.

Acknowledgment. This research was sponsored by the National Science Foundation through grants GP-6676 and GP-1977.

---

(25) D. J. Hodgson and J. A. Ibers, *ibid.*, *7*, 2345 (1968).

(26) M. P. Johnson and D. F. Shriver, *J. Amer. Chem. Soc.*, *88*, 301 (1966).

(27) H. Brunner, P. C. Waieles and H. D. Kaesz, *Inorg. Nucl. Chem. Letters*, *1*, 125 (1965).