$W(CO)_4(P(C_6H_5)_3)(NHC_5H_{10})$, 38496-27-4; *cis*-$W(CO)_4(P(C_6H_5)_3)(NC_5H_5)$, 38496-28-5; *cis*-$W(CO)_4(P(C_6H_5)_3)C(OC_2H_5)CH_3$, 38467-05-9; *cis*-$W(CO)_4(P(C_6H_5)_3)C(OC_2H_5)CH_2C_6H_5$, 38467-06-0; *cis*-$W(CO)_4(P(C_6H_5)_3)C(OC_2H_5)C_6H_5$, 38467-07-1; *cis*-$W(CO)_4(As(C_6H_5)_3)C(OC_2H_5)CH_3$, 38467-08-2; *cis*-$W(CO)_4(P(OCH_2)_3)C(C_2H_5)C(OC_2H_5)CH_3$, 38467-09-3.

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Synthesis, Reactivity, and Spectroscopic Studies of Adducts of Isoelectronic and Isostructural Analogs of *trans*-Chlorocarbonylbis(triphenylphosphine)iridium(I) with Lewis Acids

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Treatment of the complexes *trans*-$IrCl(CO)(As(C_6H_5)_3)_2$ (II), *trans*-$IrCl(CS)(P(C_6H_5)_3)_2$ (IV), and *trans*-$IrF(CO)(P(C_6H_5)_3)_2$ (V) with Lewis acids, including cyano olefins, boron halides, O_2, SO_2, and antimony halides, yields a variety of adducts. For II the O_2 and SO_2 adducts exhibit coordinated ligand reactivity. For IV the boron halide adducts undergo hydrolysis to give oxidative-addition products. A method of comparing $\Delta\bar{\nu}_{CO}$ and $\Delta\bar{\nu}_{CS}$ is advanced. On the basis of competitive reactions with the same Lewis acids, a tentative basicity order is given for II, IV, and V relative to the parent complex, *trans*-$IrCl(CO)(P(C_6H_5)_3)_2$ (I). Changes in $\Delta\bar{\nu}_{CO}$ and $\Delta\bar{\nu}_{CS}$ upon adduct formation are consistent with our transition metal basicity model. Limitations on this method are discussed.

Introduction

The parent complex *trans*-$IrClCO(P(C_6H_5)_3)_2$ (I) has been shown to undergo many diverse and interesting reactions involving oxidative addition,[2] homogeneous catalysis,[3] adduct formation with Lewis acids,[4] stabilization of molecules that do not exist at room temperature,[5] and activation of coordinated ligands.[6] Despite this extensive amount of research, the role played by the ligands in regulating the activity and basicity of complexes of type I toward Lewis acids may be of critical importance as has been indicated by recent kinetic and thermodynamic results on the rate of reversible oxygenation of metal complexes[7,8] and the activation of molecular hydrogen by metal complexes.[9]

Recently, we have become interested, in our laboratories, in investigating transition metal basicity and reactivity of metal complexes by systematically studying a group of carefully selected competitive reactions between "isostructural" and "isoelectronic" four-coordinate iridium(I) complexes and Lewis acids with a view to establish an order of relative basicity among these donors. Moreover, the strength of the interaction upon adduct formation may be estimated from the change in carbonyl stretching frequency, $\Delta\bar{\nu}_{CO}$, upon adduct formation,[4,10] assuming that the electron density is transferred from the antibonding molecular orbital of the carbonyl moiety causing an increase in the carbonyl force constant. These results serve as a check on the competitive reactions.

Although this criterion of acid strength has worked well in general, yet one must compare the reactions of isostructural and isoelectronic metal complexes with the same Lewis acid so that if the geometry of the adduct has any influence on $\bar{\nu}_{CO}$, then the complexes will be affected in the same manner.[7,10] In addition, $\Delta\bar{\nu}$'s should not be compared for adducts and oxidative-addition reactions. In certain limited cases these data are in agreement with thermodynamic parameters for these systems.[4,11]

Experimental Section

Infrared spectra in the NaCl region were measured on a Perkin-Elmer 257 grating spectrophotometer as Nujol mulls or chloroform solutions and calibrated with polystyrene. Far-infrared spectra were recorded using a Beckman IR 11. Carbon, hydrogen, and nitrogen analyses were carried out by M-H-W Laboratories, Garden City, Mich. Sulfur analysis was done by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Chlorine analysis was done by Dornis Kolbe Mikroanalytisches Laboratorium, Mulheim a.d. Ruhr, West Germany. Oxygen analysis was done by Micro-Tech Laboratories, Skokie, Ill.

trans-$IrClCO(P(C_6H_5)_3)_2$ (I) and *trans*-$IrClCO(As(C_6H_5)_3)_2$ (II) were purchased from Strem Chemicals, Inc., Danvers, Mass., and were used without further purification. *trans*-$IrClCO(As(C_6H_5)_3)_2$ was kept under nitrogen atmosphere since it reacted with atmospheric oxygen on standing. The extent of oxygen uptake is time dependent and reaches a maximum of *ca.* 20% if left indefinitely in air. To ensure the purity of the complex before performing any reaction, an infrared spectrum was recorded after heating the complex at 60° for 45 min to effect removal of any coordinated oxygen. Acrylonitrile (ACRYL), cinnamonitrile (CINNA), crotonitrile (CROTO), allyl cyanide (ALLYLCY), tetracyanoethylene (TCNE), and fumaronitrile (FUM) are Aldrich Chemical Co., Inc., products

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and were used without further purification except for the fumaronitrile which was sublimed before use. Triphenylphosphine, silver tetrafluoroborate, boron trihalides, and antimony trihalides were used without further purification. *p*-Nitrobenzoyl azide was recrystallized from acetone–water. All solvents were distilled, degassed, and dried over Linde 4A molecular sieves. The glove bag technique or Schlenk-type reaction tube was used for reactions carried out under a nitrogen atmosphere.

Preparation of Complexes. *trans*-IrCl(N$_2$)(P(C$_6$H$_5$)$_3$)$_2$ (III) was prepared by a modification of a standard procedure.[12] I (0.4 g) was cooled to 0° under nitrogen in a Schlenk-type reaction tube. Chloroform (8.0 ml at 0°) and absolute ethanol (0.15 ml) were added. Solid *p*-nitrobenzoyl azide (0.1 g or 1.05 mol relative to I) was then added with vigorous stirring. After 1 min the solution became red and then slowly changed back to yellow-orange, after which time (or 5 min) 50 ml of cold methanol was added suddenly. The solution was stirred for about 10 min and filtered (under N$_2$) and the yellow precipitate was washed twice with 5-ml portions of cold methanol and dried under a stream of dry N$_2$. The standard procedure for the preparation of the nitrogeno complex[12] III depends on the small amount of ethanol present in commercial chloroform to esterify the isocyanate intermediate. The added ethanol in this work guarantees an excess (about 5 molar excess relative to I).

***trans*-IrCl(CS)((C$_6$H$_5$)$_3$)$_2$.** The thiocarbonyl complex was prepared by a modification of a procedure first reported by Kubota and Carey.[13] The nitrogen complex, IrCl(N$_2$)(P(C$_6$H$_5$)$_3$)$_2$ (III) (0.2 g) was treated with cold CS$_2$ in a nitrogen atmosphere and the excess CS$_2$ was evaporated under a N$_2$ stream. The black or greenish-black residue, IrClC$_2$S$_5$(P(C$_6$H$_5$)$_3$)$_2$, was recrystallized from CH$_2$Cl$_2$–CH$_3$OH to give fine black microcrystals. To this was added 0.4 g of P(C$_6$H$_5$)$_3$ and 15 ml of 2:1 CHCl$_3$–CH$_3$OH. After 4 hr of gentle refluxing and stirring the solution became a deep maroon. An additional 0.1 g of P(C$_6$H$_5$)$_3$ and 5 ml of CH$_3$OH were added and the solution was refluxed for another hour. The orange crystalline complex IrCl(CS)(P(C$_6$H$_5$)$_3$)$_2$ (IV) was filtered off, washed with CH$_3$OH, and dried *in vacuo* over MgClO$_4$, yield 50% based on I. *Anal.* Calcd for IrC$_{37}$H$_{30}$ClP$_2$S: C, 55.8; H, 3.80; S, 4.03. Found: C, 55.0; H, 3.82; S, 3.87.

***trans*-IrF(CO)(P(C$_6$H$_5$)$_3$)$_2$ (V).** The fluoro complex was prepared by combination of recent reports on standard procedures.[14,15] Such a procedure produces enhanced yields and consistency. After 0.054 g (0.28 mmol) of AgBF$_4$ was dissolved in 20 ml of acetonitrile, 0.199 g (0.28 mmol) of IrClCO(P(C$_6$H$_5$)$_3$)$_2$ was added to it under a nitrogen atmosphere. Within a few minutes, the formation of the acetonitrile coordinated salts is signaled by a precipitate of AgCl. After filtering the solution and evaporating it to dryness, the residue is redissolved in 20 ml of an ammonium fluoride saturated solution of methanol and heated slightly while stirring. The fluorinated product can then be precipitated by adding an equal amount of an aqueous 0.1 *M* NH$_4$F solution, yield 91% based on I. *Anal.* Calcd for IrC$_{37}$H$_{30}$OFP$_2$: C, 58.19; H, 3.93; F, 2.49. Found: C, 58.09; H, 3.91; F, 2.21.

Preparation of the Adducts of IrCl(CO)(As(C$_6$H$_5$)$_3$)$_2$ (II). The sulfur dioxide VI, oxygen VII, and FUM 1:1 adducts were prepared by methods analogous to those in the literature for their phosphine analogs,[16-18] respectively. No C or H analysis was done for the cyano olefin adducts as there is no substantial difference in C and H content between the adducts and II. These adducts were characterized by their infrared spectra which exhibited $\bar{\nu}_{CN}$ values in close agreement with previously reported values,[18] while the rest of the bands were shifted but identical with the infrared spectrum of II. *Anal.* Calcd for IrC$_{37}$H$_{30}$ClAs$_2$SO$_3$: C, 47.6; H, 3.22; S, 3.43. Found: C, 47.6; H, 3.24; S, 2.99. Calcd for IrC$_{37}$H$_{30}$ClAs$_2$O$_2$: C, 49.3; H, 3.33; O, 5.33. Found: C, 49.12; H, 3.21; O, 5.68. Calcd for IrC$_{41}$H$_{32}$ClAs$_2$ON$_2$: N, 2.96. Found: N, 2.88.

IrCl(CO)(As(C$_6$H$_5$)$_3$)$_2$·ACRYL. ACRYL (5 ml, 75 mmol) was added to a flask containing II (0.2 g, 0.23 mmol). The bright yellow mixture lightened immediately and in 1 min a white solid began to form. After 10 min of stirring the white solid was collected on a filter and washed with benzene and hexane. Recrystallization from benzene–*n*–hexane yielded small white crystals (0.2 g, 95% yield), $\bar{\nu}_{CN}$ 2208 cm^{-1}. *Anal.* Calcd for IrC$_{40}$H$_{33}$OClAs$_3$N: N, 1.52. Found: N, 1.38.

IrCl(CO)(As(C$_6$H$_5$)$_3$)$_2$·CROTO. *trans*-CROTO (5 ml, 62 mmol) was added to a flask containing II (0.2 g, 0.23 mmol) and the mixture was heated at 60° for 1 hr. The solution did not change color but after addition of *n*-hexane, a beige solid settled, was collected on a filter, and washed with benzene and *n*-hexane. Recrystallization from benzene–*n*-hexane yielded small off-white crystals (0.18 g, 90% yield). *Anal.* Calcd for IrC$_{41}$H$_{35}$OClAs$_2$N: N, 1.50. Found: N, 1.52. $\bar{\nu}_{CN} = 2210$ cm^{-1}.

IrCl(CO)(As(C$_6$H$_5$)$_3$)$_2$·CINNA. A mixture of II (0.3 g, 0.34 mmol), CINNA (2 ml, 15 mmol), and 3 ml of benzene was warmed at 60° for 1 hr. A 1:2 ratio of benzene–hexane was then added to the oily residue to settle an olive solid which after filtering and washing with benzene and *n*-hexane was recrystallized from benzene–*n*-hexane to yield small beige crystals (0.31 g, 91% yield), $\bar{\nu}_{CN}$ 2220 cm^{-1}. *Anal.* Calcd for IrC$_{46}$H$_{37}$OClAs$_2$N: N, 1.40. Found: N, 1.56.

IrCl(CO)(As(C$_6$H$_5$)$_3$)$_2$·SbF$_3$. Solid SbF$_3$ (1.8 g, 10 mmol) was added with constant stirring to a solution of II (0.3 g, 0.34 mmol) in 10 ml of benzene. The stirring was continued for 1 hr and the excess SbF$_3$ was filtered off to yield a dark greenish supernatant liquid which after evaporation under a stream of nitrogen yielded a slightly hygroscopic olive powder (0.29 g, 81% yield). *Anal.* Calcd for IrC$_{37}$H$_{30}$OClAs$_2$SbF$_3$: C, 42.0; H, 2.87; F, 5.44. Found: C, 42.45; H, 2.69; F, 4.94.

IrCl(CO)(As(C$_6$H$_5$)$_3$)$_2$·SbCl$_3$. A solution of SbCl$_3$ (0.077 g, 0.34 mmol) in 5 ml of benzene was added to a solution of II (0.3 g, 0.34 mmol) in 10 ml of benzene. The color of the solution changed from light yellow to off-white. After the solution was stirred for 20 min *n*-hexane was added and a grayish-white, air-sensitive solid precipitated (0.31 g, 85% yield). It is important *not* to add an excess of SbCl$_3$. *Anal.* Calcd for IrC$_{37}$H$_{30}$OCl$_4$As$_2$Sb: C, 40.6; H, 2.74; Cl, 12.9. Found: C, 40.2; H, 2.68; Cl, 12.6.

IrCl(CO)(P(C$_6$H$_5$)$_3$)$_2$·SbF$_3$. This adduct was prepared by a method analogous to that used for its arsine analog *vide supra*. *Anal.* Calcd for IrC$_{37}$H$_{30}$OClP$_2$SbF$_3$: C, 46.3; H, 3.13; F, 5.95. Found: C, 46.1; H, 3.02; F, 5.40.

IrCl(CO)(P(C$_6$H$_5$)$_3$)$_2$·SbCl$_3$. This adduct was prepared also by a method analogous to that used for its arsine analog *vide supra*. *Anal.* Calcd for IrC$_{37}$H$_{30}$OCl$_4$P$_2$Sb: C, 44.0; H, 2.97; Cl, 14.0. Found: C, 44.2; H, 3.16; Cl, 14.1.

IrCl(CO)(As(C$_6$H$_5$)$_3$)$_2$·2BF$_3$. Upon addition of 1 ml of BF$_3$·O(C$_2$H$_5$)$_2$ to II (0.3 g, 0.34 mmol) there is an immediate color change from light yellow to reddish brown. After evaporation under a stream of nitrogen, a brown, hygroscopic solid was obtained (0.24 g, 72% yield). *Anal.* Calcd for IrC$_{37}$H$_{30}$OClAs$_2$B$_2$F$_6$: C, 44.3; H, 2.99; F, 11.4. Found: C, 44.5; H, 3.37; F, 11.9.

IrCl(CO)(As(C$_6$H$_5$)$_3$)$_2$·SO$_4$ (VII). This compound may be prepared by two different methods in quantitative yield. (a) IrCl(CO)(As(C$_6$H$_5$)$_3$)$_2$·O$_2$ (VII) reacts easily with SO$_2$ in solution or in the solid state to form the iridium sulfate adduct. A concentrated solution of VII in CH$_2$Cl$_2$ was treated with a small flow of SO$_2$ for 20 min. The product was precipitated by addition of methanol and was recrystallized from CH$_3$OH–CH$_2$Cl$_2$. (b) Attempts to prepare the IrCl(CO)(As(C$_6$H$_5$)$_3$)$_2$·SO$_2$ adduct in the atmosphere yielded a mixture of this moiety and the sulfate complex. If the reaction is handled in a glove bag under nitrogen, one obtains pure SO$_2$ adduct. Upon exposure to atmospheric oxygen, the color fades from green to off-white. After 24 hr one obtains the sulfate complex. *Anal.* Calcd for IrC$_{37}$H$_{30}$O$_5$ClAs$_2$S: C, 46.1; H, 3.11; S, 3.32. Found: C, 46.30; H, 3.47; S, 4.00.

Attempted Preparation of IrCl(CO)(As(C$_6$H$_5$)$_3$)$_2$·ALLYLCY and IrCl(CO)(P(C$_6$H$_5$)$_3$)$_2$·ALLYLCY. A procedure analogous to that used to prepare IrCl(CO)(As(C$_6$H$_5$)$_3$)$_2$·CROTO yielded yellow crystals identified *via* infrared as II and I, respectively.

Preparation of the Adducts of IrCl(CS)(P(C$_6$H$_5$)$_3$)$_2$ (IV). The cyano olefin adducts were prepared by direct reaction of the appropriate cyano olefin (TCNE, FUM, ACRYL) in benzene with IV. These adducts were characterized by their infrared spectrum which exhibited stretching frequencies, $\bar{\nu}_{CN}$, at 2220 and 2205, 2222 cm^{-1} for TCNE and FUM, respectively. This is in close agreement with values reported previously[18] for adducts of these acids with I.

The boron halide (BX$_3$, X = Cl, Br) adducts were prepared by freezing the trihalide onto a methylene chloride solution of the complexes I and IV, respectively, *in vacuo*. The attempted preparation

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of the boron trifluoride adduct was accomplish by the direct reaction of $BF_3 \cdot (C_2H_5)_2O$ with IV.

The hydrogen chloride oxidative-addition products were prepared by direct reaction with HCl(g) in benzene or by hydrolysis of the BCl_3 adducts of I and IV.

All analyses, except the BX_3 (X = Cl, Br) adducts, were in good agreement with calculated results.

Preparation of the Adducts of $IrFCO(P(C_6H_5)_3)_2$ (V). Preparation of the Adducts. These adducts were prepared by methods analogous to those referenced in the literature, except as noted.

No C or H analysis was done for the cyano olefin adducts as there is no substantial difference in C and H content between the adducts and IV. These adducts were characterized by their infrared spectra which exhibited $\bar{\nu}_{CN}$ values in close agreement with previously reported values,[18] while the rest of the bands were shifted but identical with the infrared spectrum of IV.

$IrF(CO)(P(C_6H_5)_3)_2 \cdot SO_2$.[16] This compound was obtained as green crystals having infrared characteristic frequencies at $\bar{\nu}_1$ S–O(sym) 1050 cm^{-1} and $\bar{\nu}_3$ S–O(asym) 1185, 1198 cm^{-1}; yield, 95%. *Anal.* Calcd for $IrC_{37}H_{30}FP_2SO_3$: C, 53.68; H, 3.62. Found: C, 53.75; H, 3.74.

$IrFCO(P(C_6H_5)_3)_2 \cdot O_2$.[17] Best results for the preparation of this adduct are obtained when the reaction is carried out under the following conditions: $[Ir] = 1 \times 10^{-3}$ *M* in CH_2Cl_2; P_{O_2} 1.5 atom; 25°, 2 hr. The adduct exhibited a $\bar{\nu}_{O-O}$ at 850 cm^{-1}; yield 74%. *Anal.* Calcd for $IrC_{37}H_{30}FP_2O_3$: C, 55.9; H, 3.7. Found. C, 56.03; H, 3.77.

$IrFCO(P(C_6H_5)_3)_2 \cdot$FUM.[18] The adduct was isolated as an off-white solid: $\bar{\nu}_{CN}$ 2223, 2212 cm^{-1}; yield, 94%. *Anal.* Calcd for $IrC_{41}H_{32}FP_2ON_2$: N, 3.33. Found: N, 3.38.

$IrFCO(P(C_6H_5)_3)_2 \cdot$TCNE.[18] The adduct was isolated as pale yellow crystals: $\bar{\nu}_{CN}$ 2230 cm^{-1}; yield, 95%. *Anal.* Calcd for $IrC_{43}H_{30}FP_2ON_4$: N, 6.29. Found: N, 6.29.

$IrFCO(P(C_6H_5)_3)_2 \cdot$ACRYL. The procedure employed for II above was used; however, the precipitation of the adduct was induced by slight evaporation of the solution with nitrogen bubbling: $\bar{\nu}_{CN}$ 2210 cm^{-1}; yield, 85%. *Anal.* Calcd for $IrC_{40}H_{33}P_2ON$: N, 1.72. Found: N, 1.88.

$IrFCO(P(C_6H_5)_3)_2 \cdot$CROTO. The procedure employed for II above was used. This adduct was obtained as a beige powder when the mixture of V and crotonitrile were heated at 80° for 90 min followed by addition of *n*-hexane: $\bar{\nu}_{CN}$ 2215 cm^{-1}; yield, 84%. *Anal.* Calcd for $IrC_{41}H_{35}FP_2N$: N, 1.69. Found: N, 1.70.

Results and Discussion

Relative Basicity of II *vs.* I. A summary of the complexes prepared with II, their carbonyl stretching frequencies, $\Delta\bar{\nu}_{CO}$, and a comparison with their phosphine analogs is given in Table I.

Reactions with Lewis Acids. The cyano olefins TCNE,[18] FUM, ACRYL, CROTO, and CINNA react with II to give 1:1 adducts. This is in contrast to a report that I does not form adducts with the weaker Lewis acids CROTO and CINNA. The fact that we are able to isolate adducts of these Lewis acids with II suggests that differences in the relative basicity, rather than kinetic factors,[18] are responsible for the failure to isolate adducts of I with these Lewis acids. However, such steric factors may be reflected in the fact that $\Delta\bar{\nu}_{CO}$ for the more acidic CINNA is less than $\Delta\bar{\nu}_{CO}$ for ACRYL.

The adducts with II appear to be stable over long periods of time, in the solid state, but dissociate partly in solution. The failure to isolate adducts of I or II with ALLYLCY indicates that the acidity of the olefin bond is not enhanced by an electron-withdrawing group adjacent to the double bond, *vis a vis* CROTO *vs.* CINNA (see Table I).

Table I. Adducts of $IrCl(CO)L_2$ with Lewis Acids

	L = $As(C_6H_5)_3$			L = $P(C_6H_5)_3$		
	$\bar{\nu}_{CO}$[a]	$\Delta\bar{\nu}_{CO}$	Ref	$\bar{\nu}_{CO}$[a]	$\Delta\bar{\nu}_{CO}$[b]	Ref
$IrClCOL_2$	1939			1960		
$IrClCOL_2$ SO_2	2007	68		2020	64	16
$IrClCOL_2 \cdot SO_4$	2053	114		2045[c]	89	6
$IrClCOL_2 \cdot 2BF_3$	2058	119		2063	107	19
$IrClCOL_2 \cdot O_2$	1992	53		2000	44	17
$IrClCOL_2 \cdot SbF_3$	2055	116		2060	100	
$IrClCOL_2 \cdot SbCl_3$	2080	141		2070	110	
$IrClCOL_2 \cdot$TCNE	2055[d]	116	11	2060[d]	105	18
$IrClCOL_2 \cdot$FUM	2022[d]	83		2029[d]	74	18
$IrClCOL_2 \cdot$ACRYL	2010	71		2017[e]	62	18
$IrClCOL_2$. CROTO	1995	56		No reaction		18
$IrClCOL_2 \cdot$CINNA	2006	67		No reaction		18
$IrClCOL_2 \cdot$ALLYLCY	No reaction			No reaction		

[a] Nujol mull unless otherwise noted; all spectra in cm^{-1}. [b] Based on values reported for referenced authors for $\bar{\nu}_{CO}$ of $IrClCO(P(C_6H_6)_3)_2$. [c] KBr disk. [d] CH_2Cl_2 solution. [e] Complex loses acrylonitrile on standing in air at room temperature.

Table II. Far-Infrared Metal–Ligand Stretching Frequencies

Complex	$\bar{\nu}_{IrCl}$[a]
trans-$IrCl(CO)(As(C_6H_5)_3)_2$	337
$IrCl(CO)(As(C_6H_5)_3)_2 \cdot SbF_3$	341
$IrCl(CO)(As(C_6H_5)_3)_2 \cdot SbCl_3$	342

[a] Reciprocal centimeters.

The change in carbonyl stretching frequency, $\Delta\bar{\nu}_{CO}$, upon adduct formation (Table I) reflects both the stability of the adduct with respect to decomposition as well as the acidity of the cyano olefin and decreases in the order TCNE > FUM > ACRYL and CINNA > CROTO. The Lewis acid BF_3 forms a 2:1 adduct with II in agreement with the report[19] of a 2:1 adduct with the parent complex I (when an excess of BF_3 is used). While a trigonal-bipyramidal structure has been proposed for the geometry of the $Pt(P(C_6H_5)_3)_3 \cdot 2BCl_3$ adduct,[20] the structure of $IrCl(CO)(P(C_6H_5)_3)_2 \cdot 2BF_3$ has not been clearly elucidated.[21]

Reaction of the strong Lewis acids SbF_3 and $SbCl_3$ with I and II yielded 1:1 adducts. The adducts with $SbCl_3$ were unstable with respect to hydrolysis, but the SbF_3 adducts are only slightly air-sensitive.

The far-infrared iridium chloride stretching frequency for II and the antimony halide adducts is given in Table II. These data indicate that halogen abstraction leading to the formation of four-coordinate antimony is not occurring. Further, the lack of extra bands mitigates against the antimony halides adding in an oxidative-addition manner. The increase in $\bar{\nu}_{IrCl}$ upon adduct formation here is consistent with a previous report[19] on the $IrCl(CO)(P(C_6H_5)_3 \cdot 2BF_3$ adduct.

Activation upon Coordination. The Lewis acids SO_2 and O_2 react with II to yield 1:1 adducts VI and VII, respectively, in agreement with previous reports[16,17] on their phosphine analogs.

During an early attempt to prepare VI, the $\bar{\nu}_{CO}$ band of the product was split ~60–80 cm^{-1}, thus precluding the type of solid state splitting reported for analogous complexes[18] (20 cm^{-1}) and indicating a mixture of products. Subsequent investigation revealed that SO_2 was reacting with both II and VII to yield VI and $IrCl(CO)(As(C_6H_5)_3)_2 \cdot$

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Table III. Infrared Absorptions of Sulfur Dioxide and Sulfate Complexes[a]

Compd	$\bar{\nu}_1$(sym)	$\bar{\nu}_3$(asym)	Ref
$IrCl(CO)(P(C_6H_5)_3)_2{\cdot}SO_2$	1048	1198, 1185	16
$IrCl(CO)(As(C_6H_5)_3)_2{\cdot}SO_2$ (III)	1048	1190, 1185	This work
$IrI(CO)(P(C_6H_5)_3)_2{\cdot}SO_4$	856	1172	*b*
$IrCl(CO)(As(C_6H_5)_3)_2{\cdot}SO_4$ (V)	855	1172	This work

[a] All spectra in cm^{-1}. [b] R. W. Horn, E. Weissberger, and J. P. Collman, *Inorg. Chem.*, 9, 2366 (1970).

Table IV. Infrared Absorptions of Iridium Adducts[a]

Compd	$\bar{\nu}_{O-O}$	$\bar{\nu}_1$ S–O(sym)	Ref
$IrCl(CO)(P(C_6H_5)_3)_2{\cdot}O_2$	857		17
$IrCl(CO)(As(C_6H_5)_3)_2{\cdot}O_2$ (IV)	857		This work
$IrI(CO)(P(C_6H_5)_3)_2{\cdot}O_2$	862		25
$IrCl(CO)(P(C_6H_5)_3)_2{\cdot}SO_2$		1048	16
$IrCl(CO)(As(C_6H_5)_3)_2{\cdot}SO_2$		1048	This work

[a] All spectra in cm^{-1}.

Table V. Adducts of $IrCl(CS)(P(C_6H_5)_3)_2$ with Lewis Acids

Lewis acid	Adduct, color	$\bar{\nu}_{CS}$, cm^{-1}	$\Delta\bar{\nu}_{CS}$, cm^{-1}
C_6N_4 (TCNE)	1:1, off-white	1370	+38
$C_4N_2H_2$ (FUM)	1:1, off-white	1350	+18
C_3NH_3 (ACRYL)	No reaction		
BCl_3	1:*n*, tan	1361	+29
BBr_3	1:*n*, tan	1377	+45
BF_3	No reaction		
C_2H_4	No reaction		

Table VI. Oxidative-Addition Products with Iridium(I) Complexes

Complex	Addendum	$\bar{\nu}_{IrH}$, cm^{-1}	$\Delta\bar{\nu}_{CO}$, cm^{-1}
$IrCl(CO)(P(C_6H_5)_3)_2$	HCl	2240	+70
$IrCl(CO)(P(C_6H_5)_3)_2$[a]	HCl	2245	+70
$IrCl(CS)(P(C_6H_5)_3)_2$	HCl	2240	+45

[a] Reference 13.

Table VII. Comparison of Changes in Stretching Frequency for Carbonyl and Thiocarbonyl Iridium(I) Adducts[a]

Lewis acid	$\Delta\bar{\nu}_{CO}$	$\Delta\bar{\nu}_{CS}$
C_6N_4 (TCNE)	100[b]	38
$C_4N_2H_2$ (FUM)	69[b]	18
BCl_3	110	18
BBr_3	110	28

[a] All cm^{-1}. [b] Reference 18.

SO_4 (VIII), respectively. This occurred since II reacts with the atmosphere to yield *ca.* 20% of VII. This report is in agreement with a previous report[3] that *trans*-$IrI(CO)(P(C_6H_5)_3)_2{\cdot}O_2$ reacts with SO_2 to yield the sulfate product. These reactions are given in eq 1.

$$\underset{\text{VII}}{\mathrm{IrCl(CO)(As(C_6H_5)_3)_2{\cdot}O_2}} + \mathrm{SO_2} \rightarrow \underset{\text{VIII}}{\mathrm{IrCl(CO)(As(C_6H_5)_3)_2{\cdot}SO_4}} \qquad (1)$$

$$\mathrm{IrI(CO)(P(C_6H_5)_3)_2{\cdot}O_2 + SO_2 \rightarrow IrI(CO)(P(C_6H_5)_3)_2{\cdot}SO_4}$$

The sulfur dioxide and sulfate complexes of iridium may be identified and characterized by their infrared spectra. The data for a series of these complexes are given in Table III.

Upon exposing VI to the atmosphere, the green color fades instantaneously and after 24 hr an off-white complex identical with VIII is obtained. This complex may also be obtained by bubbling O_2 through a benzene solution of VI for 15 min. This result should be contrasted with a report that the SO_2 adduct of I does not react with O_2. However, reactions of metal–sulfur dioxide complexes with oxygen to yield sulfate complexes have been reported,[22] *e.g.*, the platinum–sulfur dioxide complex. These reactions are summarized in eq 2.

$$\underset{\text{VI}}{\mathrm{IrCl(CO)(As(C_6H_5)_3)_2{\cdot}SO_2}} + \mathrm{O_2} \rightarrow \underset{\text{VIII}}{\mathrm{IrCl(CO)(As(C_6H_5)_3)_2{\cdot}SO_4}}$$

$$\mathrm{IrCl(CO)(P(C_6H_5)_3)_2{\cdot}SO_2 + O_2} \rightarrow \text{no reaction} \qquad (2)$$

$$\mathrm{Pt(P(C_6H_5)_3)_3{\cdot}SO_2 + O_2 \rightarrow Pt(P(C_6H_5)_3)_3{\cdot}SO_4}$$

During the course of our investigation of the oxygen adduct of II, we accidentally prepared a complex that analyzes as VII. The empirical formula agrees with the accepted dioxygen adducts of Vaska type analogs. However, this compound exhibits no O–O stretch and a very high $\bar{\nu}_{CO}$ 2075 cm^{-1}. Moreover, during this preparation, one could follow the disappearance of the normal $\bar{\nu}_{CO}$ for VII and subsequent appearance of the new band at 2075 cm^{-1} and the gradual disappearance of $\bar{\nu}_{O-O}$. One may conclude from the large $\Delta\bar{\nu}_{CO}$ and the absence of $\bar{\nu}_{O-O}$ that this moiety contains Ir(III) coordinated to a symmetrically bound O_2^{2-} and no $Ph_3P{=}O$ ligands are formed as no noticeable change was observed in the infrared to the appearance of (P=O) stretching absorptions while the rest of the bands remained the same. Such a complex is of considerable potential interest since Gray[23,24] and coworkers have proposed recently that the non-heme iron protein oxyhemerythrin contains an $Fe^{III}{-}O_2^{2-}{-}Fe^{III}$ linkage. (Regrettably, repeated attempts to reprepare the peroxide adduct of II were met with failure.)

On the basis of the competitive reactions carried out with the cyano olefins and the activation of coordinated sulfur dioxide by II, we propose that the arsine complex II is more basic than its phosphine analog I. Moreover, the spectral shifts $\Delta\bar{\nu}_{CO}$ in Table I for identical acids are in agreement with our conclusion concerning the relative transition metal basicity as larger shifts are revealed for II. Although the above proposal is in agreement with recently formulated ideas concerning "latent basicity"[10] ($\bar{\nu}_{CO}$ 1960 cm^{-1} (I) *vs.* $\bar{\nu}_{CO}$ 1939 cm^{-1} (II)), yet care must be taken[7] to compare complexes having isostructural ligands.

As a consequence of the enhanced basicity of II, one would expect a decrease in $\bar{\nu}_{O-O}$ and $\bar{\nu}_{1(S-O)}$ in the oxygen and sulfur dioxide adducts, respectively, of II compared to I. This does not occur here as is indicated in Table IV.

In the case of $\bar{\nu}_{O-O}$, Ibers[25] and coworkers have noted that this parameter seems relatively insensitive to appreciable changes in the O–O bond length and presumably the strength of the Ir–O bond.

Byrd[26] has investigated the infrared spectra of adducts of *N,N*-dimethylanilines with sulfur dioxide and has found little change in $\bar{\nu}_{1(S-O)}$ for anilines of different known base strengths in agreement with previous reports on iodine systems.[27] Consequently, these parameters seem to be insensitive indicators of relative base strength.

Relative Basicity of IV *vs.* I. We have modified a procedure for the preparation of IV first reported by Kubota and Carey,[13] according to eq 3. This complex reacts with a

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Table VIII. Adducts of $IrX(CO)P(C_6H_5)_3)_2$ with Lewis Acids

	X = F			X = Cl		
	$\bar{\nu}_{CO}{}^a$	$\Delta\bar{\nu}_{CO}$	Ref	$\bar{\nu}_{CO}{}^a$	$\Delta\bar{\nu}_{CO}{}^b$	Ref
$IrX(CO)P(C_6H_5)_3)_2$	1944			1960		
$IrX(CO)(P(C_6H_5)_3)_2 \cdot SO_2$	2010	66	This work	2020	64	16
$IrX(CO)(P(C_6H_5)_3)_2 \cdot O_2$	1990	46	This work	2000	44	17
$IrX(CO)(P(C_6H_5)_3)_2 \cdot$TCNE	2055^c	111	This work	2060^c	104	18
$IrX(CO)(P(C_6H_5)_3)_2 \cdot$FUM	2023^c	79	This work	2029^c	74	18
$IrX(CO)(P(C_6H_5)_3)_2 \cdot$ACRYL	2008	64	This work	2017^d	62	18
$IrX(CO)(P(C_6H_5)_3)_2 \cdot$CROTO	1988	44	This work	No reaction		18
$IrX(CO)(P(C_6H_5)_3)_2 \cdot$CINNA	No reaction		This work	No reaction		18

^{a} Nujol nulls unless otherwise noted; all spectra in cm^{-1}. ^{b} Based on values reported for referenced authors for $\bar{\nu}_{CO}$ of $IrCl(P(C_6H_5)_3)_2$. ^{c} CH_2Cl_2 solution. ^{d} Complex loses acrylonitrile on standing in air at room temperature.

$$\underset{\text{II}}{IrCl(N_2)(P(C_6H_5)_3)_2} \xrightarrow{CS_2} IrCl(C_2S_5)(P(C_6H_5)_3)_2 \xrightarrow[\bar{\nu}_{CS}\ 1332\ cm^{-1}]{\text{excess } P(C_6H_5)_3}$$

$$\underset{\text{IV (orange-yellow)}}{IrCl(CS)(P(C_6H_5)_3)_2} \qquad (3)$$

number of Lewis acids to give the adducts listed in Table V.

Unlike the parent complex I, IV forms 1:1 adducts only with the most acidic cyano olefins.

The stoichiometry of the adducts I and IV with BX_3 (X = Cl, Br) has not been satisfactorily characterized by us which agrees with the report from another laboratory on the adducts of I with BX_3 (X = Cl, Br).[21] These adducts are extremely unstable with respect to hydrolysis and hydrolyze to give the products listed in Table VI. These results are in agreement with those reported earlier for HCl oxidative addition[28] and may be used to characterize these complexes.

Our results with the boron halide adducts should be contrasted with a report of stable 1:1 adducts between $RhCl(CO)(P(C_6H_5)_3)_2$ and BCl_3 and BBr_3, respectively.[29]

Durkin and Schram[20] have reported recently that both 1:1 and 1:2 adducts are formed between some platinum(0) *tert*-phosphine complexes and BCl_3. They also report the formation of $P(C_6H_5)_3 \cdot BCl_3$ under certain conditions. Analyses of the "X"-sensitive vibration[30] in our studies disclose no evidence for the formation of such moieties in the reactions of IV with BCl_3.

In contrast to the parent complex I which forms 1:1 and 1:2 adducts with the weaker Lewis acid BF_3,[19] IV does not form an adduct with BF_3.

In order to see how the $\Delta\bar{\nu}$ might be expected to vary upon adduct formation, we have assumed an "isolated" quadratic potential for the carbonyl stretching motion, for which the fundamental vibration frequency is given by eq 4 where k is

$$\bar{\nu} = \frac{1}{2\pi}\sqrt{k/\mu} \qquad (4)$$

the force constant and μ is the reduced mass of the atom pair. Upon forming the differential and neglecting the term containing $d\mu$ (since the reduced masses are not affected by adduct formation) we obtain

$$d\bar{\nu} = \frac{1}{4\pi}\sqrt{1/k\mu}\, dk$$

Thus, in order to compare differential changes in $\bar{\nu}_{CO}$ and $\bar{\nu}_{CS}$ one may form the ratio

$$d\bar{\nu}_{CO}/d\bar{\nu}_{CS} = \sqrt{k_{CS}\mu_{CS}/k_{CO}\mu_{CO}}\ dk_{CO}/dk_{CS}$$

If we write this in terms of finite changes, we obtain eq 5

$$\Delta\nu_{CO}/\Delta\nu_{CS} = 0.865\kappa \qquad (5)$$

where κ represents the ratio of the change in force constants. If one assumes κ is unity, *i.e.*, constant change in the force constants upon adduct formation, the carbonyl frequency shift upon adduct formation should be 0.865 of the thiocarbonyl shift for the formation of the same adduct. If κ is assumed to be as large as 1.47, that is, equal to the ratio of the frequencies, $\bar{\nu}_{CO}/\bar{\nu}_{CS}$, then the ratio in eq 5 becomes 1.27.

Studies are in progress[31] to determine the correct theoretical value of κ.

We feel confident that regardless of the value of κ that is finally determined, $\Delta\bar{\nu}_{CS}$ (corrected) will remain less than $\Delta\bar{\nu}_{CO}$ in agreement with other parameters. A comparison of changes in stretching frequency upon adduct formation is given in Table VII.

Insofar as the decrease in chemical reactivity is an indication of diminished transition metal basicity, we propose that the thiocarbonyl complex is less basic than its carbonyl analog. Such a conclusion is substantiated by the spectral shifts in Table VII and is also in agreement with molecular orbital calculations which predict that the thiocarbonyl complex should be less basic[32] than the carbonyl complex.

Relative Basicity of V *vs.* I. On the basis of the enhanced electronegativity of fluorine relative to chlorine, one might expect decreased electron density at the metal and hence decreased reactivity and metal basicity of V relative to I. Recent reports on the rates of oxygenation and deoxygenation of *trans*-$IrX(CO)(P(C_6H_5)_3)_2$ (X = F, Cl, Br, I, NCO, $OClO_3$, N_3, ONO_2, NO_2)[8] and X-ray data[25] on the molecular oxygen adducts with *trans*-$IrX(CO)(P(C_6H_5)_3)_2$ (X = Cl, Br, I) seem consistent with the proposal that decreasing electronegativity of the halogen enhances the electron density at the metal.

However, as has been noted earlier,[14] principles of "latent basicity"[10] predict contrary arguments since $\bar{\nu}_{CO}$ = 1944 cm^{-1} for V *vs.* $\bar{\nu}_{CO}$ = 1960 cm^{-1} for I (our work); 1957 cm^{-1} (V) *vs.* 1965 cm^{-1} (I) (ref 30), in these isostructural and isoelectronic metal complexes; one concludes from total electronegativity arguments that such a phenomenon "finds a natural interpretation in terms of currently accepted theory of σ-π dualism."[14]

A summary of the complexes prepared, their carbonyl stretching frequencies, $\Delta\bar{\nu}_{CO}$, and a comparison with their chlorine analogs, is given in Table VIII.

It is interesting to note that the cyano olefins ACRYL and CROTO react with V to give stable 1:1 adducts. This is

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in contrast to a report[18] that I does not form an adduct with the weaker Lewis acid CROTO and that the adduct with ACRYL is unstable in air. Moreover, the spectral shifts $\Delta\bar{\nu}_{CO}$ reflect a slight, but consistent increase for V relative to I and, hence, increased interaction of Lewis acid and metal complex. Such a result, although surprising in terms of the electronic properties of the ligands, seems to indicate that the fluoro complex V is more basic than its chloro analog I.

A plausible explanation for this apparent enhanced basicity seems to be difficult, as it cannot be ascribed to a single factor, and probably should await further results from measurements of accurate thermodynamic parameters in nonpolar solvents.

Conclusion

On the basis of chemical reactivity data which have been presented for isostructural and isoelectronic iridium(I) complexes with Lewis acids, we propose the following tentative order of relative basicity: $IrClCO(As(C_6H_5)_3)_2 > IrClCO(P(C_6H_5)_3)_2 > IrClCS(P(C_6H_5)_3)_2$. Such reactivity seems to increase with increasing basicity of the metal center which is a function of the neighboring ligands in agreement with previous results.[8,9] The relative basicity of $IrFCO(P(C_6H_5)_3)_2$ *vs.* the parent complex cannot be decided at the moment as noted earlier.

Registry No. *trans*-$IrCl(CO)(AsPh_3)_2$, 23954-42-9; *trans*-$IrCl(CS)(PPh_3)_2$, 30106-92-4; *trans*-$IrF(CO)(PPh_3)_2$, 32356-62-0; *trans*-$IrCl(CO)(PPh_3)_2$, 15318-31-7; *trans*-$IrCl(N_2)(PPh_3)_2$, 21414-18-6; *p*-$O_2NC_6H_4CON_3$, 2733-41-7; CH_3CN, 75-05-8; $[Ir(CO)(CH_3CN)(PPh_3)_2]BF_4$, 39196-84-4; NH_4F, 12125-01-8; SO_2, 7446-09-5; O_2, 7782-44-7; $BF_3{\cdot}O(C_2H_5)_2$, 109-63-7; $IrCl(CO)(AsPh_3)_2{\cdot}SO_2$, 39111-71-2; $IrCl(CO)(AsPh_3)_2{\cdot}SO_4$, 39111-72-3; $IrCl(CO)(AsPh_3)_2{\cdot}O_2$, 39111-73-4; $IrCl(CO)(AsPh_3)_2{\cdot}SbF_3$, 39196-85-5; $IrCl(CO)(AsPh_3)_2{\cdot}SbCl_3$, 39111-74-5; $IrCl(CO)(AsPh_3)_2{\cdot}$FUM, 36483-99-5; $IrCl(CO)(AsPh_3)_2{\cdot}$ACRYL, 39040-91-0; $IrCl(CO)(AsPh_3)_2{\cdot}$CROTO, 39040-92-1; $IrCl(CO)(AsPh_3)_2{\cdot}$ALLYLCY, 39040-93-2; $IrCl(CO)(PPh_3)_2{\cdot}SbF_3$, 39111-75-6; $IrCl(CO)(PPh_3)_2{\cdot}SbCl_3$, 39196-86-6; $IrCl(CS)(PPh_3)_2{\cdot}$TCNE, 39040-94-3; $IrCl(CS)(PPh_3)_2{\cdot}$FUM, 39040-95-4; $IrCl(CS)(PPh_3)_2{\cdot}xBCl_3$, 39040-85-2; $IrCl(CS)(PPh_3)_2{\cdot}xBBr_3$, 39040-89-6; HCl, 7647-01-0; $IrHCl_2(CS)(PPh_3)_2$, 39040-90-9; $IrF(CO)(PPh_3)_2{\cdot}SO_2$, 39111-81-4; $IrF(CO)(PPh_3)_2{\cdot}O_2$, 39111-82-5; $IrF(CO)(PPh_3)_2{\cdot}$TCNE, 39151-91-2; $IrF(CO)(PPh_3)_2{\cdot}$FUM, 39040-96-5; $IrF(CO)(PPh_3)_2{\cdot}$ACRYL, 39151-92-3; $IrF(CO)(PPh_3)_2{\cdot}$CROTO, 39151-93-4.

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Reduction of Coordinated Nitrosyls. Preparation, Characterization, and Reduction of Nitrosylpentaaquochromium(2+)[1]

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A direct, quantitative, and convenient method for the preparation of $CrNO^{2+}$ has been achieved by a detailed study of the reduction of the nitrosyl complex by Cr^{2+}. The reaction of NO with Cr^{2+} is rapid and produces only $CrNO^{2+}$ provided that the NO is kept in excess over the Cr^{2+}. Addition of an excess of Cr^{2+} reduces the coordinated nitrosyl in a simultaneous two-electron step to NH_3OH^+ and the Cr dimer. The general form of the rate law for the nitrosyl reduction is $-d[CrNO^{2+}]/dt = [k_1 + k_2/H^+][Cr^{2+}][CrNO^{2+}]$. The values of k_1 (M^{-1} sec^{-1}) and k_2 (sec^{-1}) at 25.4° are 0.490 and 2.9×10^{-2}, respectively.

Introduction

On initiating our studies on the reactivity of coordinated nitrosyls, chromous ion was chosen to investigate the reducibility of a variety of metal nitrosyls. Chromous ion possesses a fairly high reduction potential and yet is sufficiently stable in acidic solutions. When oxidized, it yields substitution-inert complexes which aid in the identification of the mechanism of electron transfer. When bridging ligands are present, Cr^{2+} reductions are often quite rapid.[2] Thus, the possibility emerges that Cr^{2+} cannot only reduce the nitrosyl or the metal center but may also retain the nitrosyl function in the process of electron transfer. In order to pursue this area of interest, it was necessary to explore the previously reported $Cr(H_2O)_5NO^{2+}$.[3] Ardon and Herman[3] have reported that the oxidation of Cr^{2+} by NO_3^- or NO produces $CrNO^{2+}$ (<50%), Cr^{3+}, and the Cr dimer. In the course of our work, we have (1) improved the method of preparing $CrNO^{2+}$, (2) characterized the $CrNO^{2+}$ complex further, and (3) studied in detail the kinetics and stoichiometry of the reduction of $CrNO^{2+}$ by Cr^{2+}.

Experimental Section

Reagents. $LiClO_4$ was made by the method of Olson.[4] The Li^+ concentration was determined by adding an aliquot of $LiClO_4$ to a column containing Dowex 50W-X8, 200–400 mesh, in the acid form. (The resin was cleaned according to the method of Deutsch.[5]) After washing the column with water, the acid in the eluent was determined by titration with a standard NaOH solution. Chromium(II) perchlorate solutions were prepared by the reduction of the chromium(III) salt with amalgamated zinc under a stream of argon. Stock solutions of chromium(III) perchlorate were prepared by reduction of primary standard $K_2Cr_2O_7$ with acidic H_2O_2 and boiling the solu-

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