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Calorimetric Study of the Lewis Acid Properties of Coordinatively Unsaturated Organoiridium(III) Species

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The Lewis acid character of a series of coordinatively unsaturated iridium(III) complexes of the type $\{IrCl_2R[P(C_6H_5)_3]_2\}$ (R is $C(O)CF_nH_{3-n}$ (n = 1, 2, or 3), $-S(O)_2R'$ (R′ = CH_3, C_2H_5, or CF_3), or CH_3) has been studied by calorimetric and spectroscopic methods. Enthalpy data for addition of pyridine as a function of R are interpreted in terms of a trans influence series for the R groups. This thermochemical trans influence series is compared with that derived from the trends in iridium–chlorine stretching frequencies in model compounds having R trans to Cl. The enthalpy change and equilibrium constant for pyridine addition to the complex in which R = $C(O)CF_3$ were determined in six solvents. The trends in enthalpy changes and equilibrium constants for addition of a series of ten bases to the trifluoroacetyl complex in methylene chloride are interpreted in terms of base strength and steric factors. The enthalpy change for pyridine addition to $\{IrClXCH_3[P(C_6H_5)_3]_2\}$ (X = Cl, Br, –NCO, NO_2, or CH_3CO_2) in methylene chloride reveals that the cis influence of X is low. Representative examples of the octahedral adducts $\{IrCl_2R[P(C_6H_5)_3]_2\cdot B\}$ have been isolated and characterized. In each case the base B is found to add stereospecifically trans to the substituent R.

We wish to report the results of a thermochemical study of the interaction of five-coordinated iridium(III) complexes with Lewis bases. The Lewis acid character of a coordinatively unsaturated metal–ligand fragment, ML_{N-1} (N = normal coordination number of the metal ion), determines the nature of the interaction between the metal and the Nth ligand, B, in $L_{N-1}M$–B. Understanding this interaction is a central pursuit in the study of reaction mechanisms,[1] homogeneous catalytic properties,[2] thermodynamics,[3] and synthesis[4] of coordination compounds. The coordinatively unsaturated species is ubiquitous in coordination chemistry but by its nature is usually a reactive intermediate and difficult to study.[5] The usual circumstance in the study of reactions of Lewis bases with metal complexes leads to thermodynamic parameters for a ligand substitution process[6] which can be broken down into the two steps shown in eq 1. The measured enthalpy change,

$$L_{N-1}M{-}L' \rightarrow L_{N-1}M + L' \tag{1a}$$

$$L_{N-1}M + B \rightarrow L_{N-1}M{-}B \tag{1b}$$

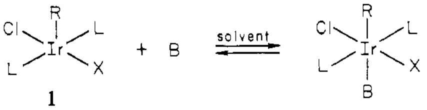
$$\Delta H_{\text{exptl}} = \Delta H_{1b} + H_{1a} \tag{2}$$

for example, is a composite of two contributions, shown in eq 2, which cannot in general be separated.[7] This complication has been overcome in a few cases. Graddon and his co-workers have obtained thermodynamic data for an extensive series of four-coordinate complexes of nickel, copper, or zinc which add Lewis bases to give five- or six-coordinated products.[8] Poyntz and co-workers have studied the reaction of bis(triphenylphosphine)platinum(0) with unsaturated molecules by calorimetric methods.[9] In these cases the metal undergoes an increase in coordination number and the new base does not displace a ligand from the coordination sphere. Drago has reported a method which will, in favorable circumstances, allow separation of dimer–monomer enthalpy changes from overall heats of reaction and applied it to the determination of the heats of reaction of the coordinatively unsaturated species $\{Co(CH_3)(DMG)_2\}$ (DMG = dimethglyoximato ion),[10] $\{Rh(CO)_2Cl\}$,[11] and $\{Rh(1,5\text{-}C_8H_{14})Cl\}$[12] with bases. A set of relative displacement enthalpies can be determined when a series of bases is added to the same metal complex, if a common ligand is displaced in each reaction. This method has been used with nitrile complexes of palladium,[13] olefin complexes of platinum[14] and rhodium[15], and a tetrahydrofuran complex of platinum.[16] The bonding capabilities of coordinatively unsaturated species have been approached from a theoretical point of view by Elian and Hoffmann.[17]

The effects of ligands already in the ML_{N-1} fragment on the interaction of the metal and the Nth ligand have been divided into the cis and trans influence depending on the position of the ligand in question with respect to the Nth ligand. These have been discussed from both an empirical and theoretical point of view.[18-20] To date direct thermochemical evidence for the magnitudes of these two interactions is not available. Experimental evidence for the trans influence rests primarily on metal–ligand bond stretching frequencies in the IR, chemical shifts and coupling constants in the NMR, and bond length data from x-ray diffraction studies.[18,19] Attempts to derive trans influence series from equilibrium or enthalpy data for ligand-exchange reactions is complicated by the inseparability of the contributions of processes 1a and 1b. Williams and co-workers[21] have found a correlation between trans influences measured by the change in $\nu(C{\equiv}N)$ as X is varied in cobinamides of the type *trans*-$(XCo(N_4)CN)$ and equilibrium constants for replacement of water in *trans*-$(XCo(N_4)H_2O)$. In general, however, the relationship between spectral parameters used to measure the trans influence and the corresponding thermodynamic parameters is not known. The most direct measure of cis or trans influences would be the enthalpy change for reaction 1b, determined in a solvent of low basicity.

A series of five-coordinated iridium(III) complexes having the general formula $\{IrClXR[P(C_6H_5)_3]_2\}$ (X = anion and R = H,[22] $C(O)R'$,[23-26] $-S(O)_2R''$,[27,28] or CH_3[29]) has been prepared and characterized. They are monomeric in solution, and all available evidence is consistent with the complexes having a square-pyramidal structure with the organo ligand, R, in the apical position. This is in accord with predictions based on theoretical calculations for five-coordinated, d^6 complexes.[30,31] Single-crystal x-ray diffraction has shown $\{Rh(CH_3)I_2[P(C_6H_5)_3]_2\}$[32] and $\{RuCl_2[P(C_6H_5)_3]_3\}$[33] to have square-pyramidal geometries. The extent to which such coordinatively unsaturated complexes may interact with weakly basic organic solvent molecules in solution is not known.

The iridium complexes have been found to add a variety of Lewis bases. In all systems studied the base adds, stereospecifically, trans to the group R as shown in eq 3.[22-29] This



1 2 (3)

$L = P(C_6H_5)_3$

series of compounds provides a unique opportunity to sys-

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tematically obtain thermodynamic data on the trans influence of a series of R groups, the cis influence of anions X, the Lewis base strength of a series of ligands, B, toward a coordinatively unsaturated metal site, and the effect of solvents on the acid–base reaction.

Experimental Section

The compounds (where L = $P(C_6H_5)_3$) $\{IrCl_2[C(O)CF_3]L_2\}$,[25,26] $\{IrCl_2[C(O)CF_nH_{3-n}]L_2\}\cdot 0.5\ CH_2Cl_2$ ($n = 1$ or 2),[25] $\{IrCl_2[S(O)_2R]L_2\}$ (R = CH_3, C_2H_5,[27] or CF_3[28]), and $\{IrClX(CH_3)L_2\}$ (X = Cl, Br, NCO, NO_2, or CH_3CO_2)[29] were prepared by methods in the literature. Nitrogen bases were distilled from potassium hydroxide pellets and stored in a desiccator. Trimethyl phosphite (Stauffer Chemical), dimethylformamide, dimethyl sulfoxide, and acetonitrile were distilled before use. Tetrahydrofuran was stored over calcium hydride and distilled before use. Benzene was distilled and stored over molecular sieves. Other solvents were distilled from P_4O_{10} prior to use. Infrared spectra were run on a Perkin-Elmer Model 621 spectrometer. NMR spectra were run on Varian HA-100 and T-60 spectrometers. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. In those cases where calculated and found values agreed within 0.5% only the symbols of the elements analyzed are given.

$\{IrCl_2[C(O)CF_nH_{3-n}][P(C_6H_5)_3]_2B\}$ (n = 1, 2, or 3, B = C_5H_5N; n = 3, B = $P(OCH_2)_3CC_2H_5$). The acyl complex, 100 mg, was suspended in benzene, 2 mL, and 2 drops of pyridine (or 0.2 g of the phosphite) was added with vigorous stirring. The orange suspension became light cream colored over 2–3 min. The precipitate was recovered, washed with ether, and dried in vacuo; yield ca. 100 mg. Pyridine complexes: $n = 1$, mp 252–255 °C: Anal. ($C_{43}H_{37}Cl_2FNOP_2Ir$) C, H. IR (Nujol, cm^{-1}) ν(C=O) 1645 (s), 1635 (sh); ν(IR—Cl) 310 (w). $n = 2$, mp 174 °C: Anal. Calcd for $C_{43}H_{36}Cl_2F_2NOP_2Ir$: C, 56.40; H, 3.84. Found: C, 55.18; H, 4.12. IR (Nujol, cm^{-1}) ν(C=O) 1645 (s), 1633 (sh); ν(Ir—Cl) 306 (w). $n = 3$, mp 235–240 °C: Anal. Calcd for $C_{43}H_{35}Cl_2F_3NOP_2Ir$: C, 53.58; H, 3.71. Found: C, 54.72; H, 3.68. IR (Nujol, cm^{-1}) ν(C=O) 1635 (s); ν(Ir—Cl) 325 (w). ^{19}F NMR ($CDCl_3$, C_6F_6) 90.7 ppm downfield from C_6F_6 (s, C(O)CF_3). B = $P(OCH_2)_3CC_2H_5$, $n = 3$, mp 162–164 °C: Anal. ($C_{44}H_{41}Cl_2F_3O_4P_3Ir$) C, H, Cl. IR (Nujol, cm^{-1}) ν(C=O) 1660 (s); ν(Ir—Cl) 321 (w).

$\{IrCl_2(CH_3)[P(C_6H_5)_3]_2\cdot B\}$ (B = C_5H_5N, $(CH_3)_2SO$, or $P(OCH_2)_3CC_2H_5$). The methyl complex, $\{IrCl_2CH_3[P(C_6H_5)_3]_2\}$, 150 mg, was added to dimethyl sulfoxide, 2 mL. After 40 min of stirring the light cream precipitate was recovered, washed with ether, and dried in vacuo; yield 140 mg. The Me_2SO-d_6 complex was prepared in the same way. The pyridine complex was prepared from 170 mg of methyl complex by the same method used for the acyl complexes, yield 150 mg, as was the phosphite complex which was recrystallized from methylene chloride–ether; yield 130 mg. B = $(CH_3)_2SO$, mp 156–158 °C: Anal. ($C_{39}H_{39}Cl_2SOP_2Ir$) C, H. IR (Nujol, cm^{-1}) ν(S=O) 955 (m); $\delta(CH_3)$ 930 (m), 990 (s); ν(Ir—Cl) 319 (w). B = $(CD_3)_2SO$: IR (Nujol, cm^{-1}) ν(S=O) 960 (m). B = C_5H_5N, mp 191–193 °C: Anal. ($C_{42}H_{38}Cl_2NP_2Ir$) C, H. IR (Nujol, cm^{-1}) ν(Ir—Cl) 310 (w). B = $P(OCH_2)_3CC_2H_5$, mp 277–280 °C: Anal. Calcd for $C_{43}H_{44}Cl_2O_3P_3Ir$: C, 53.53; H, 4.56; Cl, 7.35. Found: C, 52.62; H, 4.81; Cl, 7.07. IR (Nujol, cm^{-1}) ν(Ir—Cl) 320 (w).

$\{IrCl_2[C(O)CF_3][P(C_6H_5)_3]_2[HC(O)N(CH_3)_2]\}\cdot HC(O)N(CH_3)_2$. The trifluoroacetyl complex, 120 mg, was stirred in 3 mL of dimethylformamide for 1.5 h. The resulting light yellow, crystalline solid was recovered, washed with ether, and dried in vacuo at room temperature for 24 h; yield 120 mg. Upon prolonged exposure (72 h) to a dynamic vacuum the crystals gradually turn orange which is indicative of the removal of coordinated DMF. The solid gradually turns orange above 100 °C. Anal. ($C_{44}H_{44}Cl_2F_3O_3N_2P_2Ir$) C, H, N. IR (Nujol, cm^{-1}) 1683 (vs), 1643 (s), 1625 (vs); ν(Ir–Cl) 320 (m).

$\{IrCl_2[C(O)CF_3][P(C_6H_5)_3]B_2\}$ (B = C_5H_5N or C_4H_8S). B = C_4H_8S. The trifluoroacetyl complex, 100 mg, was added to 1 mL of tetrahydrothiophene and the resulting yellow solution stirred for 1.5 h. Ether, 5 mL, was added and the solution refrigerated (−20 °C) overnight. The resulting yellow crystalline precipitate was recovered, washed with ether, and dried in vacuo; yield 70 mg.

B = C_5H_5N. The trifluoroacetyl complex, 60 mg, and 0.3 mL of pyridine were dissolved in 3 mL of methylene chloride. After 24 h of stirring the methylene chloride was allowed to evaporate and ether, 5 mL, was added to the remaining oil. After the mixture stood for 4 h, fine yellow needles formed. These were recovered, washed with ether, and dried in vacuo; yield 50 mg.

B = C_4H_8S, mp 137–140 °C: Anal. ($C_{46}H_{46}Cl_2F_3OS_2P_2Ir$) C, H, Cl, S. IR (Nujol, cm^{-1}) ν(C=O) 1645 (vs); ν(Ir—Cl) 325 (m). B = C_5H_5N, mp 174–176 °C: Anal. ($C_{48}H_{40}Cl_2F_3ON_2P_2Ir$) C, H, Cl, N. IR (Nujol, cm^{-1}) ν(C=O) 1642 (vs); ν(Ir—Cl) 325 (w). NMR ($CDCl_3$, C_6F_6) 89.0 ppm downfield from C_6F_6 (s, C(O)CF_3).

$\{IrCl_2[S(O)_2CF_3][P(C_6H_5)_3]_2\}$. Trifluoromethanesulfonyl chloride, 0.15 mL, and dry toluene, 10 mL, were condensed onto 540 mg of *trans*-$\{IrCl(N_2)[P(C_6H_5)_3]_2\}$ at 77 K. The mixture was warmed to 0 °C and stirred for 10 min. The resulting brown precipitate was recovered, washed with cold toluene and pentane, and then dried in vacuo; yield 330 mg; mp 141–144 °C. Anal. Calcd for $C_{37}H_{30}Cl_2F_3O_2P_2Ir$: C, 48.26; H, 3.28; Cl, 7.81; S, 3.49; mol wt 921. Found: C, 48.31; H, 3.51; Cl, 8.33; S, 4.22; mol wt ($CHCl_3$) 930. IR (Nujol, cm^{-1}) $\nu_a(SO_2)$ 1280 (s); $\nu_s(SO_2)$ 1075 (s); ν(Ir–Cl) 330 (w).

Calorimetry. Calorimetric titrations were carried out using a Tronac, Inc., 450-4 isoperibole calorimeter with constant delivery rate, 2-mL micrometer syringe, and 50-mL reaction vessel. Thermograms were recorded on a Leeds and Northrup XL-680 recorder and voltages were monitored with a 4 1/2 digit Data Technology Model 40 multimeter. The general procedure was to dissolve 10–20 mg of metal complex in 40 mL of solvent in the reaction vessel and to add an excess of 0.1–0.2 M base solution via the micrometer syringe. This was usually 0.2–0.3 mL. Enthalpy changes were calculated directly from the thermogram. The heats of dilution of metal complex and base were negligible so no correction was made in the observed heat of reaction. The standard heater was periodically calibrated vs. the heat of reaction of 0.100 N hydrochloric acid (Benco) and tris(hydroxymethyl)aminomethane, THAM. Observed values were, for example, −11.45 ± 0.23 and −11.31 ± 0.22 kcal/mol (lit.[34] −11.35 kcal/mol).

Equilibrium constants were calculated from the thermograms using the method derived by Barthel.[35] Enthalpy and equilibrium constant data are listed in Tables I–IV.

Spectrophotometric Determination of Equilibrium Constants for Reaction of $\{IrCl_2[C(O)CF_3][P(C_6H_5)_3]_2\}$ with DMF, Me_2SO, or CH_3CN. A Beckman Model 25 spectrophotometer was used to measure acid–base equilibrium constants. An ethylene glycol–water solution was circulated through the cell compartment with a Haak FK10 constant-temperature circulator. The temperature was varied from −10 to +25 °C and maintained constant (±0.2 °C) during the duration of an experiment. The temperature was measured directly in the cell compartment with a YSI Model 42SC Tele-Thermometer accurate to 0.5 °C. The cuvettes were matched Beckman Pyrex cells. The general procedure was to prepare two acid solutions of equal concentrations, one containing excess base and the other containing no base. A total of 2 mL of the pure acid solution was equilibrated in the sample compartment and the absorbance at 415 nm (λ_{max} of the acid) was recorded. Successive 20-μL additions of the second acid solution containing excess base were then added to the sample cell, and after equilibration the absorbance change was noted. The 20-μL additions were made with an Oxford micropipet known to be accurate to within 0.5%. The data were treated by the method described by Drago[36] and by an independent method as a check.

Briefly, the second procedure[37] is based on the relation

$$\Delta A = \Delta A_{max}[B]_f/(1/K + [B]_f)$$

where ΔA is the difference between the absorbance of a solution containing the iridium complex plus base and that of a solution containing only an equal concentration of complex, ΔA_{max} is the maximum absorbance charge obtainable at high [B], and $[B]_f$ is the equilibrium concentration of the added base. The data were analyzed by linearizing the relationship to give

$$\Delta A = \Delta A_{max} - (1/K)(\Delta A/[B]_f)$$

and plotting ΔA vs. $\Delta A/[B]_f$. Values of the equilibrium constant were the same by both procedures. The enthalpy changes were obtained from the temperature dependence of K. These data are given in Table V.

Results

Characterization of the Acid–Base Adducts. The reaction system of interest is summarized by eq 3. The reaction between the five-coordinate complex, **1**, and base is complete in the time of mixing. Qualitatively, the extent of reaction can

Table I. Effect of the Base on Thermodynamic Parameters for the Addition of Base to $\{IrCl_2[C(O)CF_3][P(C_6H_5)_3]_2\}$ in Methylene Chloride

B	$-\Delta H$, kcal/mol	K, L/mol (25 °C)	$-\Delta S$, eu	$-\Delta H_{corr}$,[a] kcal/mol
$P(OCH_2)_3CC_2H_5$	23.4 ± 0.9	>10^6		
$P(OCH_3)_3$	21.0 ± 0.6	(1.1 ± 0.3) × 10^5	47	22.8 ± 0.6
$CH_3S(O)CH_3$	18.4 ± 0.4	1.09 ± 0.01[b]	62	
$4\text{-}CH_3C_5H_4N$	18.6 ± 0.3	(8.4 ± 0.4) × 10^5	35	20.5 ± 0.3
$HC(O)N(CH_3)_2$	17.9 ± 0.8	26.12 ± 0.67	54	
C_5H_5N	17.7 ± 0.9	(2.5 ± 0.5) × 10^5	35	19.8 ± 0.9
CH_3CN	16.9 ± 0.2	54.5 ± 1.7[b]	50	
$C_5H_{10}NH$	12.0 ± 0.6	(2.1 ± 0.4) × 10^4	21	13.9 ± 0.6
$(C_2H_5)_2NH$	3.7 ± 0.2	(2.9 ± 0.5) × 10^4	−7.9	
C_4H_8O	≤4.4 ± 1.3[c]			
$P(C_6H_5)_3$		0		
$2\text{-}CH_3C_5H_4N$		Very low		
C_4H_8S		Very low		

[a] Corrected for base-solvent interaction by the method described in ref 10. [b] At 20 °C. [c] This value was obtained by taking the difference between the average ΔH_{corr} for pyridine and the enthalpy change for the reaction of the iridium complex with pyridine in THF as solvent (see text).

Table II. Effect of the Axial Substituent R on the Thermodynamic Parameters for Addition of Pyridine or Phosphites to $\{IrCl_2R[P(C_6H_5)_3]_2\}$ in Dichloromethane and upon Values of ν(C≡O) and ν(Ir–Cl) in Complexes in Which R Is Trans to Carbon Monoxide or Chloride

	$-\Delta H$, kcal/mol				
R	C_5H_5N	$P(OCH_2)_3CC_2H_5$	$P(OCH_3)_3$	ν(IrCl), cm^{-1}	ν(C≡O), cm^{-1}
$C(O)CF_3$	17.7 ± 0.9	23.4 ± 0.9	21.0 ± 0.6	253 ± 2[a]	2070 ± 2[a]
CH_3	17.5 ± 0.9	29.3 ± 0.8	26.7 ± 0.9	242[b]	2033[c]
$C(O)CF_2H$	16.3 ± 0.1	19.1 ± 0.6		253[a]	2079[a]
$S(O)_2CH_3$	14.8 ± 0.5			284[d]	2072[d]
$S(O)_2C_2H_5$	13.8 ± 0.4				
$S(O)_2CF_3$	12.3 ± 0.5				2100[e]
$C(O)CFH_2$	11.8 ± 0.9	16.8 ± 0.4		249[a]	2064[a]
$\{IrC_6H_4P(C_6H_5)_2)\text{-}Cl_2[P(C_6H_5)_3]\}_2$	2.7 ± 1[f] 3 + 1		0.3 ± 0.2[f]		

[a] See ref 25. [b] See ref 23. [c] See ref 29. [d] See ref 27. [e] See ref 28. [f] These values refer to the heats of addition of base to the dimeric, ortho-metalated complex. The equilibrium constants are <10^3 L/mol.

Table III. Solvent Effect on the Thermodynamic Parameters for the Addition of Pyridine to $\{IrCl_2[C(O)CF_3][P(C_6H_5)_3]_2\}$

Solvent	$-\Delta H$, kcal/mol	$-\Delta H_{corr}$,[a] kcal/mol	$10^{-5}K$, L/mol (25 °C)
CH_2Cl_2	17.7 ± 0.9	19.8	2.9 ± 0.4
$CHCl_3$	17.1 ± 0.2	21.0	2.6
$1,2\text{-}C_2H_4Cl_2$	19.0 ± 0.2	20.0	5.8
C_6H_6	17.6 ± 1.1		5.0
C_6H_5Cl	16.3 ± 0.2		5.6
C_4H_8O	16.0 ± 0.4		

[a] Corrected for the base–solvent interaction by the procedure described in ref 10.

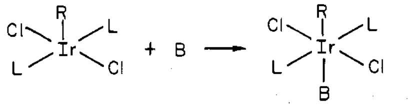
Table IV. Dependence of the Enthalpy Change for the Addition of Pyridine to $\{IrClXCH_3[P(C_6H_5)_3]_2\}$ on the Anion X, Determined in Dichloromethane

X	$-\Delta H$, kcal/mol	X	$-\Delta H$, kcal/mol
Cl	17.5 ± 0.9	CH_3CO_2	13.9 ± 0.9
Br	17.3 ± 0.3	NO_2	7.4 ± 0.8
-NCO	18.3 ± 0.4		

Table V. Equilibrium Constants for Reaction of $\{IrCl_2[C(O)CF_3][P(C_6H_5)_3]\}$ with Acetonitrile, Dimethyl Sulfoxide, and Dimethylformamide in Dichloromethane

T, K	K, L/mol	T, K	K, L/mol
$(CH_3)_2SO$			
280.5	4.87 ± 0.10	290.5	1.48 ± 0.02
283.0	3.65 ± 0.05	294.1	1.09 ± 0.01
286.8	2.35 ± 0.02		
$(CH_3)_2NC(O)H$			
278.0	158 ± 6	286.8	57 ± 3
280.5	103 ± 4	289.8	36 ± 1
283.0	78 ± 3	294.1	26 ± 1
CH_3CN			
278.0	211 ± 18	286.8	85 ± 3
280.5	161 ± 8	290.8	55 ± 2
283.0	124 ± 6		

be monitored visually since the coordinatively unsaturated species are colored and adducts are pale yellow or colorless.[24-28] Many examples of the six-coordinated adducts, **2**, have been characterized in previous work. These include pyridine, benzonitrile, and carbon monoxide adducts of $\{(IrCl_2(\text{-}S(O)_2R)[P(C_6H_5)_3]_2\}$ (R = CH_3 or C_2H_5);[27] carbon monoxide adducts of $\{IrCl_2R[P(C_6H_5)_3]_2\}$ (R = CH_3 or $C(O)CF_nH_{3-n}$; n = 1, 2, or 3);[25,29] and the dimethylformanide (DMF) complex $\{IrCl_2[C(O)CF_2H][P(C_6H_5)_3]_2DMF\}$.[25] A related series of adducts, $\{IrHCl_2[P(C_6H_5)_3]_2B\}$, having the geometry shown for compound **2** was obtained by adding a wide range of Lewis bases to $\{IrHCl_2[P(C_6H_5)_3]_2\}$.[22] As part of this study we have isolated the representative set of adducts, **3a–h**, shown in eq 4. Analytical data, included in the Experimental Section, confirm the 1:1 stoichiometry. The remaining structural features of the adducts are elucidated by their IR spectra. Each adduct shows a single band in the region 310–325 cm^{-1} which can be assigned to ν(Ir–Cl) for mutually trans chloro ligands.[18,25] The two triphenylphosphine ligands are believed to remain trans in **3a–h**. Octahedral iridium complexes having cis $P(C_6H_5)_3$ ligands are very rare.[38] The relative intensity of the two weak bands, observed in **3a–h** at 1675 (vw) and 1688 (w) cm^{-1}, has been used to infer trans geometry of the phosphines in a number of previous cases.[27,39] Trans chlorides and trans phosphines require the added base to be trans to the R group. The value of ν(C═O) for the acyl group in adducts of the trifluoroacetyl complex is decreased in going from the



(4)

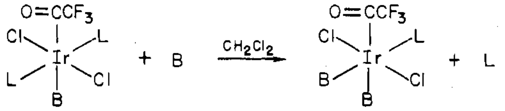
3

L = $P(C_6H_5)_3$
3, R = $C(O)CF_nH_{3-n}$; B = C_5H_5N
a, $n = 1$
b, $n = 2$
c, $n = 3$
3d, R = CH_3; B = C_5H_5N
3e, R = $C(O)CF_3$; B = $P(OCH_2)_3CC_2H_5$
3f, R = CH_3; B = $P(OCH_2)_3CC_2H_5$
3g, R = $C(O)CF_3$; B = $HC(O)N(CH_3)_2$
3h, R = CH_3; B = $CH_3S(O)CH_3$

five- (ν(C=O) is 1665 cm^{-1})[25] to the six-coordinated complexes but is not particularly sensitive to the nature of the added base, the range being 1635 (B = C_5H_5N) to 1660 cm^{-1} (B = $P(OCH_2)_3CC_2H_5$).

The dimethylformamide complex, **3g**, is isolated from DMF as a solvate with formula $\{IrCl_2[C(O)CF_3][P(C_6H_5)_3]_2DMF\}\cdot DMF$. In the ν(C=O) region of the IR spectra there is a band at 1683 cm^{-1} (free DMF, ν(C=O) 1682 cm^{-1})[40] assigned to the lattice solvent molecule, a band at 1643 cm^{-1} assigned to the trifluoroacyl group, and a broad band at 1625 cm^{-1} assigned to coordinated DMF. The decrease in ν(C=O) of DMF on coordination is indicative of the metal–oxygen bonded linkage isomer.[41] The dimethyl sulfoxide complex $\{IrCl_2CH_3[P(C_6H_5)_3]_2\cdot(CH_3)_2SO\}$, **3h**, and its $(CD_3)_2SO$ analogue were both prepared. The Me_2SO complex has bands at 990, 955, and 930 cm^{-1} which are in the region where ν(S=O) for the O-bonded form is normally found.[42] The Me_2SO-d_6 complex has only one band in this region at 960 cm^{-1} which is assigned to ν(S=O). The bands at 990 and 930 cm^{-1} are C–H modes.

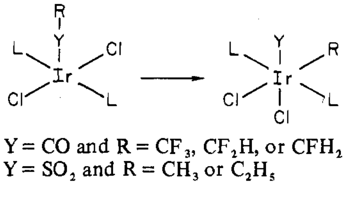
Two examples of complexes in which a second mole of base replaces a triphenylphosphine ligand, eq 5, have been isolated, where B = C_5H_5N and C_4H_8S. These complexes are characterized by a single IR band in the ν(Ir–Cl) region at 325 cm^{-1} (Cl trans to Cl).[18,25] There is a slight upfield shift in the ^{19}F NMR resonance from that of the monoaddition product and diminished intensity of the IR band at 1090 cm^{-1}, which is a triphenylphosphine mode.[43] The half-life for the addition of the second mole of base is on the order of 15–20 min when base:Ir ratio is greater than about 10:1. This was qualitatively established by the rate of appearance of the ^{19}F resonance characteristic of the bispyridine adduct.



(5)

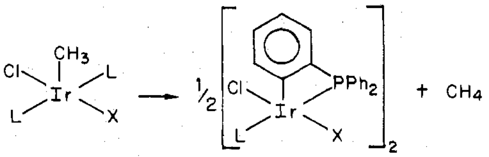
L = $P(C_6H_5)_3$
B = C_5H_5N or C_4H_8S

Some of the five-coordinated complexes used in this study can undergo the migration reactions represented in eq 6 (L = $P(C_6H_5)_3$). Kinetic data are available[25,27] which establishes that these reactions do not occur to a significant extent during the time required for a calorimetric experiment (ca. 15–30 min) at 25 °C. When R = CH_3 and X = Cl or Br, an ortho-metalation reaction has been found to occur, eq 7 (L = $P(C_6H_5)_3$). A kinetic study of this reaction has been carried out, and first-order rate constants for 25 °C are $k = 1.1 \times 10^{-4}$ s^{-1} (X = Cl) and 2.0×10^{-4} s^{-1} (X = Br).[29] This reaction will account for about 10% loss of five-coordinate complex during a calorimetry experiment, but the data can be corrected for this using the above rate constants. For X = OCN, NO_2, and CH_3CO_2 the ortho metalation is so slow that no correction is necessary.[29]



(6)

Y = CO and R = CF_3, CF_2H, or CFH_2
Y = SO_2 and R = CH_3 or C_2H_5



(7)

Thermochemistry. The thermodynamic parameters in Tables I–IV refer to the reaction represented by eq 3. The acid $\{IrCl_2[C(O)CF_3][P(C_6H_5)_3]_2\}$ was studied with the widest range of bases. Data were obtained by spectrophotometric or calorimetric methods. The bases acetonitrile, dimethyl sulfoxide, and dimethylformamide have a low equilibrium constant for association with the trifluoroacetyl complex. These constants were evaluated spectrophotometrically at temperatures between 5 and 25 °C (Table V) using the method of data treatment described by Drago.[36] The results were checked by an independent method described in the Experimental Section. Equilibrium data could not be obtained for the sulfur donors diethyl sulfide, tetramethylene sulfide, or tetramethylthiourea due to the occurrence of a side reaction in which triphenylphosphine is displaced (see eq 5). Qualitative observations indicate that the equilibrium constant for association of sulfur donors with the trifluoroacetyl complex is small (ca. $K < 10$). No detectable absorbance changes occurred in solutions of the trifluoracetyl complex upon addition of large excesses of triphenylphosphine or 2-picoline, indicating that the equilibrium constants are very low for these bases also. The data for the remaining bases listed in Table I were determined by calorimetric titrimetry.

Titration curves for the reaction of nitrogen or phosphorus donors with the five-coordinate complexes are characteristic of reactions having equilibrium constants greater than 10^4 L/mol.[44] Accordingly, enthalpy changes were calculated directly from the thermograms as were the equilibrium constants.[35] Enthalpy data for reaction of C_5H_5N, $P(OCH_3)_3$, and $P(OCH_2)_3CC_2H_5$ with five-coordinate complexes $\{IrCl_2R[P(C_6H_5)_3]_2\}$ are given in Table II. For the case in which R = CH_3 the extent of the ortho-metalation reaction shown in eq 7 was corrected for by calculating the concentration of methyl complex remaining at the time of base addition using the known rate constants for reaction 7.[29] This was usually >85% of the starting amount when the elapsed time was <25 min. The calculated amount of methyl complex and number of moles of base added at the end point usually agreed within ±5%. Thermodynamic parameters for the addition of pyridine to $\{IrCl_2[C(O)CF_3][P(C_6H_5)_3]_2\}$ in several solvents are given in Table III and enthalpies for addition of pyridine to $\{IrClXCH_3[P(C_6H_5)_3]_2\}$, where X is varied, are given in Table IV. Attempts were made to obtain data for the heat of addition of pyridine to the hydride complex $\{IrCl_2H[P(C_6H_5)_3]_2\}$ but reproducible enthalpy changes were not obtained in benzene or methylene chloride.

Discussion

The five-coordinated iridium(III) complexes used in this study, $\{RIrClX[P(C_6H_5)_3]_2\}$, function as Lewis acids toward a variety of bases. For reasons already covered in the Introduction, the acid species are believed to be square pyramidal in structure with R at the apex. That the acceptor site is trans to the group R has been established for a large number of adducts in this and previous work. The acceptor site is expected to be sterically crowded since it is cis to two triphenylphosphine ligands which have large cone angles (145°).[16] The crystal structure of $RuCl_2[P(C_6H_5)_3]_3$ shows that the vacant axial site can be blocked by an α hydrogen on a phenyl ring,[33] but no such interaction is observed in $\{RhI_2CH_3[P(C_6H_5)_3]\}_2$.[32] In both structures the metal is located above the plane of the four basal ligands.[32,33] The extent of interaction of the acid site with solvents that are very weak Lewis bases is not known. Many examples of compounds in which chlorocarbon or aromatic solvents are incorporated into the lattice of crystalline complexes of the platinum metals are known, but there is no evidence for direct coordination to the metal by these solvents.[45]

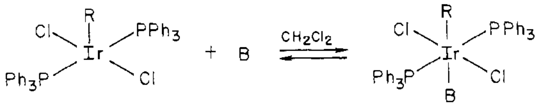
The complex dichlorotrifluoroacetylbis(triphenylphosphine)iridium(III), $\{IrCl_2[C(O)CF_3](PPh_3)_2\}$, was chosen for study in most detail since it is convenient to synthesize and undergoes no significant side reactions at 25 °C. Enthalpy changes for its reaction with pyridine were measured in six solvents (see Table III). Of the solvents used only tetrahydrofuran, THF, is normally considered to have appreciable basicity. The equilibrium constant for association of THF with $\{IrCl_2[C(O)CF_3]L_2\}$ is apparently low since solutions of this complex in THF are orange, indicating that the five-coordinate species is present.

The solvation-corrected enthalpies, ΔH_{corr}, for the pyridine reaction in the acidic solvents, CH_2Cl_2, $CHCl_3$, and 1,2-$Cl_2C_2H_4$ were obtained using the ESP procedure suggested by Drago and co-workers.[10,46] This leads to an enthalpy of -19.8 ± 0.9 kcal/mol for the pyridine–trifluoroacetyl complex interaction. The lower enthalpy change, −15.6 kcal/mol, for the reaction in tetrahydrofuran reflects the competition between THF and pyridine for the acid coordination site. The difference between this value and the solvent-corrected enthalpy sets a lower limit on the magnitude of the enthalpy change for the THF–trifluoroacetyliridium complex interaction. This value is $\Delta H \leq -4.2$ kcal/mol. The same procedure was used by Courtright et al. to estimate the enthalpy for the interaction of THF with methylcobaloxime.[10] The enthalpies measured in benzene and chlorobenzene are lower than those in chlorocarbon solvents, but these are very weak bases and not generally considered to enter into a simple acid–base reaction with a two-electron acceptor site.

The reaction of the trifluoroacetyliridium complex with a series of bases in methylene chloride gave the following order of $-\Delta H$ values, Table I: $P(OCH_2)_3CC_2H_5 > P(OCH_3)_3 >$ $4\text{-}CH_3C_5H_4N \geq CH_3S(O)CH_3 \geq HC(O)N(CH_3)_2 \geq CH_3CN$ $\geq C_5H_{10}NH > (C_2H_5)_2NH >> P(C_6H_5)_3$ or $2\text{-}CH_3C_5H_5N$. In this series the contributions of base strength and steric factors to the enthalpy changes cannot be separated. There is an inverse relation between the anticipated steric bulk of the nitrogen and phosphorus donors and the equilibrium constants for their association with the five-coordinated complex. An exception is acetonitrile which has both a low K and low steric demands. The reverse of the apparent base strengths, as measured by ΔH, of trimethyl phosphite and the cage phosphite from the order suggested by Verkade and co-workers[47] may be a steric effect. The cone angles for these ligands are $P(OCH_3)_3$, 107°, and $P(OCH_2)_3CC_2H_5$, 101° (the latter is assumed to be the same as that for the *n*-propyl analogue).[6] The order pyridine > piperidine > diethylamine is the reverse of the basicity toward protons[48] but would also be inversely related to the steric demands of the bases. Steric factors are also evident in the very small equilibrium constants for the triphenylphosphine and 2-picoline reactions.

The divergence of the equilibrium constants found for the bases listed in Table I is an intriguing feature of the data. The constants for the Me_2SO, DMF, and acetonitrile reactions with $\{IrCl_2[C(O)CF_3][P(C_6H_5)_3]_2\}$ are three or more orders of magnitude smaller than those of the pyridine, amine, and phosphite reactions. A similar trend was noted for the reaction of methylcobaloxime with oxygen vs. nitrogen or phosphorus donors and was attributed to the requirement of a specific orientation of the oxygen donor with respect to the acid complex in order to minimize steric repulsions.[10] This could conceivably account for the behavior of DMF and Me_2SO in the iridium examples but certainly not that of acetonitrile. As was the case in the cobalt system,[10] the low equilibrium constants result from very unfavorable entropy terms (Table I). A plausible explanation may lie in the fact that all three bases which display small equilibrium constants have highly polar donor functions, i.e., $>S{=}O$, $>C{=}O$, and $-C{\equiv}N$. The resulting acid–base adducts would be more polar than the pyridine, amine, or phosphite adducts and therefore are expected to demand a greater solvation by the methylene chloride. This solvation would introduce an additional exothermic contribution to the enthalpy change but would make a negative contribution to the entropy term which is the dominant effect lowering the equilibrium constants.

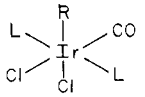
Enthalpy changes for a reaction of the type shown in eq 8



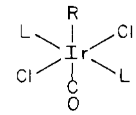
(8)

are a direct measure of the trans influence of the group R on the iridium–B bond. Steric effects will be nearly constant throughout the series in which only R is varied as will be the cis influence since the four ligands cis to the added base are not altered. Heats for the addition of pyridine and two phosphites are given in Table II. The trans-influence series based on these data is $C(O)CFH_2 > S(O)_2CF_3 > S(O)_2C_2H_5$ $> S(O)_2CH_3 > C(O)CF_2H > CH_3 > C(O)CF_3$. The position of the trifluoromethanesulfinato group in the series is not certain since there is evidence that in solutions of the five-coordinate complex there may be a facile equilibrium between S-bonded and O,O′-bidentate forms; hence addition of pyridine would require opening a chelate ring.[28] This is apparently not a complication in the alkylsulfinato complexes.[27,49] In all cases the pyridine adduct has an S-bonded sulfinato group.[27,28]

The thermodynamic trans influence series can be compared to that derived from ν(Ir—Cl) and ν(C≡O) data for the structurally similar compounds A and B (where L = P-$(C_6H_5)_3$). Iridium–chlorine stretching frequencies for chlorine trans to R in compound A and ν(C≡O) for the carbonyl group in compound B are included in Table II. The trans influence of R as measured by ν(Ir–Cl) is $CH_3 > C(O)CFH_2 >$ $C(O)CF_2H \approx C(O)CF_3 > S(O)_2R$. It can be seen that the range of values is small, 42 cm^{-1}, and that ν(Ir—Cl) is not as sensitive to the trans R group as the enthalpy change for base addition. Interpretation of the infrared data can also be complicated by coupling or lattice effects. The most outstanding difference between the calorimetric and infrared trans influence orders is in the position of the methyl group. It is near the bottom of the trans influence order in the calorimetric series and has the greatest trans influence as measured by ν(Ir—Cl).



A

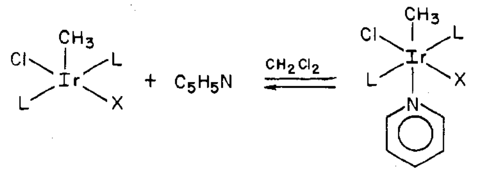


B

The methyl group differs from the acyl and sulfonyl groups in that it functions only as a σ donor while the latter two ligands have empty orbitals of π symmetry.[50,51] Pyridine and the phosphite ligands also have donor atoms with empty orbitals of π symmetry so when trans to the acyl or sulfonyl groups there can be competition for metal π-electron density. The methyl group will not compete with the trans base for the π-electron density, consequently a stronger iridium–base interaction can result. For pyridine (a weak π acceptor) the difference between the enthalpy change for R = CH_3 and $CF_3C(O)$ is not significant, but for the phosphites (good π acceptors)[52] the enthalpy change is about 6 kcal/mol more exothermic for the methyl complex. The qualitative observations that *trans*-$\{[CF_3C(O)](CO)IrCl_2L_2\}$[25] (L = $P(C_6H_5)_3$) readily loses carbon monoxide in solution while *trans*-$\{(CH_3)(CO)IrCl_2L_2\}$[29] does not can be accounted for in the same way.

It is not unusual for different probes of the trans influence of a group to give different trends.[18,19] Table II also includes values of $\nu(C{\equiv}O)$ for complexes of type B where carbon monoxide is trans to the R groups used in this study. The carbonyl stretching frequencies do not correlate with either the enthalpy changes or $\nu(Ir{-}Cl)$.

In the methyl complexes $\{IrClXCH_3[P(C_6H_5)_3]_2\}$ the anion X cis to the vacant coordination site can be varied,[29] eq 9. The



(9)

dependence of the enthalpy changes for pyridine addition on this variable is a measure of the cis influence of X. The data are given in Table IV. The trend in values, –NCO > Cl > Br > O_2CCH_3 > NO_2, may reflect slight steric or inductive effects. The two anions with significantly lower enthalpy changes, nitrite and acetate, are capable of functioning as bidentate ligands. In the solid-state, IR spectra establish that the acetate group does act as a bidentate ligand in $\{IrCl(O_2CCH_3)(CH_3)[P(C_6H_5)_3]_2\}$ and a monodentate ligand in the carbon monoxide adduct.[29] The IR spectrum of the nitrite complex $\{IrCl(NO_2)(CH_3)[P(C_6H_5)_3]_2\}$ is complex and solid samples appear to contain a mixture of linkage isomers. This is also suggested by the NMR spectrum of solutions.[29] The less exothermic ΔH values may therefore indicate that a monodentate–bidentate equilibrium is competative with pyridine addition.

Drago has had success in fitting enthalpy change data to a four-parameter equation, $-\Delta H = E_aE_b + C_aC_b$, and has obtained E and C parameters for a few group 8 metal–Lewis acid species.[10-12] This has not been possible for the trifluoroacetyl complex $\{IrCl_2[C(O)CF_3][P(C_6H_5)_3]_2\}$ for which we have the most enthalpy change data. Those data which we consider solvation-minimized enthalpies (Table I) do not provide a wide enough range of C_b/E_b values to warrant a calculation of the acid parameters. The apparently large role played by steric factors further precludes a quantitative separation of enthalpies into E_a and C_a contributions and the very large negative entropy changes observed in the DMF, Me_2SO, and acetonitrile reactions suggest that solvation effects may also play an important role in the acid–base reactions.

Qualitatively, the slope and intercept of a plot of $-\Delta H/C_b$ vs. E_b/C_b indicate a large E_a/C_a ratio which would mean that the acceptor site trans to the trifluoroacetyl group is "hard", in the Pearson classification.[11,53] Forster has presented evidence based on equilibrium constants that the "hardness" of the acceptor site in iridium(III) complexes can depend on the trans group and that both "hard" and "soft" sites can be present in the same complex.[54] A more quantitative characterization of the nature of the acceptor site in coordinatively unsaturated triarylphosphine complexes would be desirable in understanding their role in homogeneous catalysis but will not be possible until more is known about solvent and steric effects.

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Registry No. **3a**, 63599-43-9; **3b**, 63599-44-0; **3c**, 63588-85-2; **3d**, 63588-86-3; **3e**, 63588-87-4; **3f**, 63588-88-5; **3g**, 63609-12-1; **3h**, 63588-89-6; $IrCl_2(CH_3)[P(C_6H_5)_3]_2{\cdot}(CD_3)_2SO$, 63588-90-9; $IrCl_2[C(O)CF_3][P(C_6H_5)_3](C_5H_5N)_2$, 63588-91-0; $IrCl_2[C(O)CF_3][P(C_6H_5)_3](C_4HgS)_2$, 63609-40-5; $IrCl_2[S(O)_2CF_3][P(C_6H_5)_3]_2$, 63588-92-1; *trans*-$\{IrCl(N_2)[P(C_6H_5)_3]_2\}$, 21414-18-6; $IrCl_2[C(O)CFH_2][P(C_6H_5)_3]_2$, 54657-61-3; $IrCl_2[C(O)CF_2H][P(C_6H_5)_3]_2$, 54657-60-2; $IrCl_2[C(O)CF_3][P(C_6H_5)_3]_2$, 54676-79-8; $IrCl_2CH_3[P(C_6H_5)_3]_2$, 63312-66-3; $IrCl_2S(O)_2CH_3[P(C_6H_5)_3]_2$, 36448-04-1; $IrCl_2S(O)_2C_2H_5[P(C_6H_5)_3]_2$, 36530-49-1; $\{\overline{IrC_6H_4P}(C_6H_5)_2Cl_2[P(C_6H_5)_3]\}_2$, 63588-93-2; $IrClBrCH_3[P(C_6H_5)_3]_2$, 63312-67-4; $IrCl(NCO)CH_3[P(C_6H_5)_3]_2$, 63312-69-6; $IrCl(CH_3CO_2)CH_3[P(C_6H_5)_3]_2$, 63239-01-0; $IrCl(NO_2)CH_3[P(C_6H_5)_3]_2$, 63312-71-0; $P(OCH_2)_3CC_2H_5$, 824-11-3; $P(OCH_3)_3$, 121-45-9; $CH_3S(O)CH_3$, 67-68-5; 4-$CH_3C_5H_4N$, 108-89-4; $HC(O)N(CH_3)_2$, 68-12-2; CH_3CN, 75-05-8; $C_5H_{10}NH$, 110-89-4; $(C_2H_5)_2NH$, 109-89-7; C_4H_8O, 109-99-9; C_5H_5N, 110-86-1.

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New Mixed Metal Chain Complexes of Platinum(II) with Copper(II), Cobalt(II), Nickel(II), Zinc(II), Uranium(VI), and Thorium(IV) Having Substituted Phosphonito Groups as Bridging Ligands[1,2]

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Complexes $PtCl[OP(OMe)_2][HOP(OMe)_2]L$ (L = PEt_3, PPh_3) are acidic and the proton bonded to oxygen can be removed by titration with sodium methoxide or 1,5-diazabicyclo[4.3.0]non-5-ene. The resulting anionic compound will chelate to copper(II), cobalt(II), dioxouranium(VI), and thorium(IV) through the oxygens to give mixed metal compounds $\{PtCl[OP(OR)_2]_2L\}_nM$ (n = 2, R = Me, L = PEt_3, M = Cu, UO_2 and L = PPh_3, M = Co; n = 2, R = Ph, L = PEt_3, M = Cu; n = 4, R = Me, L = PPh_3, M = Th). The complex $PtCl[OP(OMe)_2][F_2BOP(OMe)_2]PEt_3$ can be prepared by treating $PtCl[OP(OMe)_2][HOP(OMe)_2]PEt_3$ with $BF_3{\cdot}Et_2O$. Mixed metal trimetallic compounds are also obtained by treating the compounds $Pt[OP(OMe)_2]_2$(L–L) with the appropriate metal salt (L–L = 1,2-bis(diphenylphosphino)ethane (dppe), *o*-phenylenebis(dimethylarsine)(diars)). Complexes $[\{Pt[OP(OMe)_2]_2(L–L)\}_2M](ClO_4)_2$ (M = Cu, Zn, L–L = dppe, diars; M = Ni, Co, L–L = dppe) have been prepared. Electronic spectra of the mixed metal complexes show a square-planar geometry about copper(II) and nickel(II) and a tetrahedral geometry about cobalt(II). The cobalt(II) complexes show unusually low extinction coefficients for the visible and near-infrared bands, although with Racah parameter B values in the 650–700-cm^{-1} range the explanation for the low extinction coefficients is likely distortion rather than highly ionic character about Co(II). Electron paramagnetic resonance spectra of complexes $\{PtCl[OP(OMe)_2]_2PPh_3\}_2Cu$ and $[\{Pt[OP(OMe)_2]_2dppe\}_2Cu](ClO_4)_2$ show resolved resonances for $g_\perp$ and hyperfine structure for $g_\|$. Calculated Δ/δ from these data is 0.676, which is in agreement with a square-planar geometry about copper(II). The complex $\{PtCl[OP(OMe)_2]_2PPh_3\}_2Co$ shows resolved resonances for $g_\|$, $g_\perp$, and $g_\perp'$, which is in agreement with elongation and twist distortion from tetrahedral geometry about Co(II). The complex $[\{Pt[OP(OMe)_2]_2dppe\}_2Cu](ClO_4)_2$ has a magnetic moment μ_{eff} of 1.89 μ_B, and a plot of $1/\chi$ against T shows that the solid follows Curie–Weiss behavior over the range 4.3–31.6 K. This result confirms that there is no interlayer coupling between copper atoms in the molecules. The magnetic moment for $\{PtCl[OP(OMe)_2]_2PPh_3\}_2Co$ is 4.49 μ_B, and again a plot of $1/\chi$ against T shows that Curie–Weiss behavior is very closely obeyed. The compounds $Pt(OPPh_2)_2(HOPPh_2)_2$ and $Pt[OP(OMe)_2]_2[HOP(OMe)_2]_2$ are dibasic acids, and for the latter complex a conductivity curve against added sodium methoxide solution shows separate breaks for K_1 and K_2.

The problem of synthesizing mixed metal chain oligomers with different metal ions in specific ligand sites has challenged coordination chemists for a long period of time. One potential method is to use a solution of a bifunctional ligand in the presence of a mixture of different metal ions and to then separate and purify the mixed metal complexes formed. This inelegant method invariably leads to poor yields of mixed metal product, even after carrying out tedious separation procedures. A more rational approach is to use a bifunctional ligand having widely discrepant coordination stabilities to the separate metals and then to coordinate the second metal to a kinetically inert complex of the first one. This approach has been used by two groups of workers with metallo-2,4-pentanedionato type ligands. Lewis has prepared a number of C-bonded 2,4-pentanedionato complexes of platinum(II) having the ligand in the keto form and has then proceeded to insert the second metal ion into chelating sites between pairs of oxygens of the C-bonded 2,4-pentanedionate.[3] A series of complexes of similar type has been prepared in an elegant manner by Lukehart.[4] These authors used the approach of building a similar type of chelate ligand, except that now the first metal is part of the ring system bidentate "metallo" 2,4-pentanedionato ligand. This structural moiety is formed by nucleophilic attack on a coordinated carbonyl group, and the second metal ion is subsequently inserted to give the mixed metal complex. Our approach is to use a P-bonded substituted phosphonito ligand as the first complex and then to coordinate the second metal into the chelating oxygen site. In this article we describe our synthetic work leading to the isolation of linear mixed metal chain compounds and present spectroscopic evidence for the geometric arrangements about the metal centers along the chain.

Phosphinous and phosphonous acids, R_2POH and $(RO)_2POH$, can exist in two tautomeric forms, one with the phosphorus in a formal trivalent state and one in the pentavalent state. When R = Me or Ph the predominant tautomeric form is the one with the phosphorus formally pentavalent.[5] These compounds and their conjugate bases are potentially ambidentate although platinum metal complexes are formed by coordination through phosphorus.