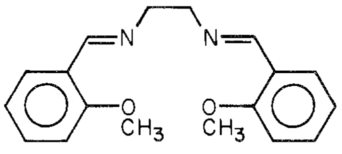
V illustrates dramatically the operation of the macrocyclic



V

effect. Whether in solution or in the solid, the open-chain ligand V shows no evidence of coordinating as a quadridentate ligand toward nickel;[27] it is bidentate using only the two nitrogen atoms as donors.

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Registry No. Ni(*O*-en-*N*-en)Br_2, 52442-21-4; Ni(*O*-en-*N*-en)I_2, 52442-23-6; Ni(*O*-en-*N*-en)$(NCS)_2$, 54484-47-8; Ni(*O*-en-*N*-pn)Br_2, 52442-27-0; Ni(*O*-en-*N*-pn)I_2, 52442-29-2; Ni(*O*-en-*N*-pn)$(NCS)_2$, 54484-48-9; Ni(*O*-en-*N*-tn)Cl_2, 52613-91-9; Ni(*O*-en-*N*-tn)Br_2, 52613-92-0; Ni(*O*-en-*N*-tn)I_2, 52613-93-1; Ni(*O*-en-*N*-tn)$(NCS)_2$, 54484-46-7; Ni(*O*-en-*N*-phen)I_2, 52442-35-0; Ni(*O*-en-*N*-phen)$(NCS)_2$, 54484-45-6; Ni(*O*-tn-*N*-en)Br_2, 52442-22-5; Ni(*O*-tn-*N*-en)I_2, 52442-24-7; Ni(*O*-tn-*N*-en)$(NCS)_2$, 54484-44-5; Ni(*O*-tn-*N*-pn)I_2, 52442-30-5; Ni(*O*-tn-*N*-pn)$(NCS)_2$, 54484-43-4; Ni(*O*-tn-*N*-tn)Cl_2, 52659-69-5; Ni(*O*-tn-*N*-tn)Br_2, 52659-70-8; Ni(*O*-tn-*N*-tn)I_2, 52659-71-9; Ni(*O*-tn-*N*-tn)$(NCS)_2$, 54484-42-3; Ni(*O*-tn-*N*-phen)Br_2, 52442-34-9; Ni(*O*-tn-*N*-phen)I_2, 52442-36-1; Ni(*O*-tn-*N*-phen)$(NCS)_2$, 54484-41-2; *O*-en, 52118-10-2; *O*-tn, 17954-12-0; *O*-en-*N*-tn, 52026-37-6; *O*-tn-*N*-tn, 51950-95-9; salicylaldehyde, 90-02-8; 1,3-dibromopropane, 109-64-8; 1,2-dibromoethane, 106-93-4; 1,3-diaminopropane, 109-76-2; Ni(trans-MC)$(NCS)_2$, 54484-49-0.

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Kinetic, Thermodynamic, and Spectral Study of Fluorine-Substituted Acetyl and Methyl Complexes of Iridium(III)

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Five- and six-coordinated acyl complexes having the formula $IrCl_2[C(O)CF_nH_{3-n}][P(C_6H_5)_3]_2$ (n = 1 or 2) and $IrCl_2[C(O)CF_nH_{3-n}](CO)[PCH_3(C_6H_5)_2]_2$ (n = 1, 2, or 3) have been prepared for the first time. The five-coordinated complexes undergo an alkyl group migration reaction upon heating in solution or as a solid to give new six-coordinated complexes, $IrCl_2(CF_nH_{3-n})(CO)[P(C_6H_5)_3]_2$. They reversibly add carbon monoxide in solution and form adducts with dimethylformamide. New trifluoromethyl complexes, $IrXICF_3(CO)[PCH_3(C_6H_5)_2]_2$ (X = Cl or Br), have been prepared via an oxidative addition reaction of trifluoromethyl iodide. The ir, ^1H and ^{19}F NMR, and electronic spectra of series of iridium(III) complexes containing the fluorine-substituted acyl group, $C(O)CF_nH_{3-n}$, and fluorine-substituted methyl group, CF_nH_{3-n} (where n = 3, 2, 1, or 0), have been studied to determine the effect of fluorine substitution in methyl and acetyl groups on the physical and chemical properties of both five- and six-coordinated complexes. The trans influence of acetyl groups, evaluated from ν(Ir–Cl) data, decreases with increasing fluorine substitution. The trans influence of the substituted methyl group decreases in the order $CH_3 > CHF_2 \approx CH_2F > CF_3$. The kinetics of the migration reaction in which the five-coordinated acyl complexes are converted to six-coordinated alkyl–carbonyl complexes have been studied in toluene. The rate of the migration decreases in the order $CFH_2 > CF_3 > CF_2H$. Calorimetric measurements for the same compounds establish that the enthalpy change for the migration becomes less exothermic in the order $CF_3 > CF_2H > CFH_2$. The calorimetric data allow determination of an approximate value for the difference between Ir–CF_3 and Ir–CH_3 bond strengths. A combination of the calorimetric and kinetic data is used to predict activation parameters for insertion of carbon monoxide into metal–fluorocarbon bonds.

Stable transition metal complexes containing acyl groups, –C(O)R, as ligands are useful as models for intermediates postulated to occur in a variety of catalytic and stoichiometric reactions of transition metal complexes.[1] Of particular significance are the coordinatively unsaturated iridium(III) complexes $IrCl_2[C(O)R][P(C_6H_5)_3]_2$, where R is a substituted benzyl group,[2] $IrCl_2[C(O)CF_3][P(C_6H_5)_3]_2$,[3] and similar rhodium(III) complexes which have been reported (see ref 4

Table I. Infrared Data (cm^{-1})[a]

No.	Compd[b]	ν(C≡O) CH$_2$Cl$_2$	ν(C≡O) Nujol	ν(C=O) CH$_2$Cl$_2$	ν(C=O) Nujol	$\nu(CF_n)$[c]	ν(Ir–Cl)[c]	Other[c]
	$IrCl_2[C(O)R](CO)L'_2$							
Ia	R = CF_3	2073	2065	1692	1695	1185, 1130	312, 260	880 ν(C(O)–C)
Ib	R = CHF_2	2070	2062	1665	1670	1060, 1035	306, 258	825 ν(C(O)–C)
Ic	R = CH_2F	2070	2060	1654	1650	932	308, 245	
Id	R = CH_3	2063	2060	1636	1625		309, 238	
	$IrCl_2[C(O)R]L_2$							
IIa	R = CF_3			1679	1665	1190, 1145	335	891 ν(C(O)–C)
IIb	R = CHF_2			1689	1681	1120, 1055	325[d]	835 ν(C(O)–C)
IIc	R = CH_2F			1692	1685	910	325	
IId	R = CH_3			1660[g]				
	trans-$IrCl_2(CO)[C(O)R]L_2$[e]							
IIIa	R = CF_3	2070		1658				
IIIb	R = CHF_2	2079		1662				
IIIc	R = CH_2F	2064		1652				
	$IrCl_2R(CO)L_2$							
IVa	R = CF_3[f]	2085	2080			1040, 1015	318, 273	283
IVb	R = CHF_2	2078	2076			1010, 962	207, 257	281
IVc	R = CH_2F	2060	2058			930, 915	305, 258	
IVd	R = CH_3	2048	2050,[g] 2026				302, 242[g]	
Va	$IrClICF_3(CO)L'_2$	2069	2080			1040, 1021	316	270
Vb	$IrBrICF_3(CO)L'_2$	2070	2080			1040, 1020		270
	$IrClICF_3(CO)L_2$[f]					1035, 1015	308	262
VI	$IrCl_2[C(O)CF_2H][HC(O)N(CH_3)_2]L_2$				1619, 1634, 1645	1110, 1030	311	

[a] Deviation ±3 cm^{-1}. [b] $L' = PCH_3(C_6H_5)_2$ and $L = P(C_6H_5)_3$. [c] Sample run as a Nujol mull. [d] Samples recrystallized from CH_2Cl_2 show one band at 325 cm^{-1}. Samples recrystallized from C_6H_6 show bands at 339 and 323 cm^{-1}. [e] CO trans to C(O)R. [f] D. M. Blake, S. Shields, and L. Wyman, *Inorg. Chem.*, 13, 1595 (1974). [g] M. Kubota and D. M. Blake, *J. Am. Chem. Soc.*, 93, 1368 (1971).

Table II. NMR Data

Compd[a]	τ-(PCH_3)[b]	τ-(CHF_n)	$\delta(CHF_n)$[c]	J(H–F), Hz
$IrCl_2[C(O)R](CO)L'_2$				
R = CH_3	7.50 t	9.34 s		
R = CFH_2	7.52 t	7.17 d	−207.2 t	50.0
R = CF_2H	7.58 t	5.25 t	−122.6 d	56.2
R = CF_3	7.65 t		−79.7 s	
$IrCl_2[C(O)R]L_2$				
R = CFH_2		5.87 d	−191.6 t	49.0
R = CF_2H		4.09 t	−116.5 d	56.0
R = CF_3			−70.2 s	

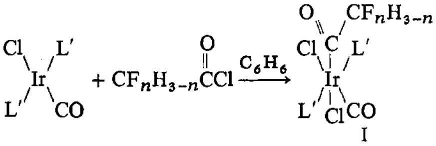
[a] $L' = PCH_3(C_6H_5)_2$ and $L = P(C_6H_5)_3$. [b] The splitting of the triplet, measured between the outside peaks, is 10 Hz. [c] ^{19}F resonances were measured with respect to internal C_6F_6 as standard and then converted to shifts with respect to $CFCl_3$ by adding −162.9 ppm.

and references therein). These complexes serve as models for reactive intermediates which have been postulated but not usually isolated in carbon monoxide insertion or decarbonylation reactions. Kinetic studies of the migration reaction of the substituted phenylacetyl complexes of iridium[2] and rhodium[4] gave some insight into the electronic factors which influence the rate at which alkyl groups migrate in metal complexes. Electron-withdrawing substituents on the phenyl ring were found to retard the rate of migration of the benzyl group.[2,4] A calorimetric study of the migration reaction in the iridium complexes $IrCl_2[C(O)R][P(C_6H_5)_3]_2$ (R = p-$O_2NC_6H_4CH_2$, p-$CH_3C_6H_4CH_2$, p-$CH_3OC_6H_4CH_2$, and CF_3) gave the first values available for the enthalpy change of a migration reaction. There is a trend toward an increasingly exothermic enthalpy change as the electronegativity of the benzyl substituent increases. The enthalpy change for the trifluoromethyl group is nearly 6 times the magnitude of that for the benzyl groups. The average value for the benzyl groups is −14.8 kJ/mol compared to −85.0 kJ/mol for the trifluoromethyl group.[5]

In order to investigate the factors which influence the rate and thermochemical parameters for the migration reaction in coordinatively unsaturated iridium(III)–acyl complexes new five- and six-coordinated complexes containing fluorine-substituted acetyl, $C(O)CF_nH_{3-n}$, and methyl, CF_nH_{3-n}, groups (n = 0, 1, 2, or 3) have been prepared and characterized. A number of examples of acetyl and methyl complexes (n = 0) of iridium have been prepared via the oxidative addition of acetyl or methyl halides[6-8] to iridium(I) complexes. This method has been used to prepare trifluoromethyl[7] and trifluoroacetyl[3,7,8] complexes but has not been extended to mono- and difluoro analogs. Manganese[9] and cobalt[10] complexes containing the acyl groups having formula $C(O)CF_nH_{3-n}$ (n = 0, 1, 2, or 3) have been prepared via the reaction of acyl halides with metal carbonyl anions.

Results

Acetyl and Fluorine-Substituted Acetyl Complexes. The reaction of the complex *trans*-chlorocarbonylbis(methyldiphenylphosphine)iridium(I) with acetyl chloride or fluorine-substituted acetyl chlorides gave the octahedral iridium(III) complexes shown in eq 1.



(1)

I

$L' = PCH_3(C_6H_5)_2$
a, $n = 3$
b, $n = 2$
c, $n = 1$
d, $n = 0$

Compound Id has previously been reported.[7] The infrared spectra of compounds Ia–d (Table I) show a strong, terminal carbonyl band at ca. 2070 cm^{-1}, a band due to ν(C=O) of the acyl group, 1630–1692 cm^{-1}, and two bands due to ν(Ir—Cl), one between 306 and 312 cm^{-1} and another in the range of 238–262 cm^{-1}. The former is due to chlorine trans to carbon monoxide and the latter to chlorine trans to the acyl group.[3] Bands due to the CF_n vibrational modes lie between 900 and 1200 cm^{-1}. ^1H NMR spectra (Table II) show a triplet for the PCH_3 group indicating trans phosphine ligands.[7,11] In addition the resonances for the protons of the CF_nH_{3-n} group appear as a triplet for Ib and a doublet for Ic due to H–F

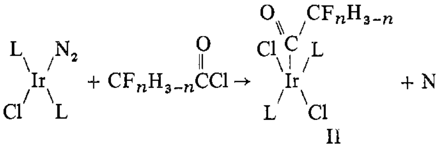
Table III. Electronic Spectra of Five-Coordinate Acyl Complexes

Complex[a]	Wavelength at max,[b] nm	Molar absorptivity, M^{-1} cm^{-1}
$IrCl_2[C(O)CFH_2]L_2$	407.1	407
	489.3	343
$IrCl_2[C(O)CF_2H]L_2$	407.4	476
	477.5	356
$IrCl_2[C(O)CF_3]L_2$	418.8	464
	491.2	295

[a] $L = P(C_6H_5)_3$. [b] Toluene solution.

coupling. ^{19}F NMR spectra show a singlet for Ia, doublet for Ib, and triplet for Ic.

The complex *trans*-chlorodinitrogenbis(triphenylphosphine)iridium(I) reacts with an acyl chloride in benzene or toluene to give five-coordinated acyl complexes as is shown in eq 2.



(2)

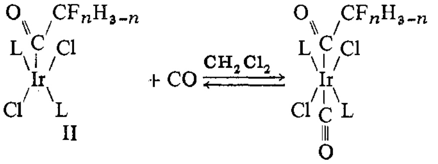
II

$L = P(C_6H_5)_3$
a, $n = 3$
b, $n = 2$
c, $n = 1$

Compound IIa has been previously reported,[3] but additional data are included here. As has been reported,[6] the unsubstituted acetyl analog of compounds IIa–c is unstable with respect to a migration reaction in which it is converted to the six-coordinate complex $IrCl_2(CO)CH_3[P(C_6H_5)_3]_2$. Attempts to isolate the five-coordinate complex by reaction of the dinitrogen complex with neat acetyl chloride at 0° gave only the methyl–carbonyl complex. It appears that the migration reaction rate is comparable to that of the initial oxidative addition step. The ν(C═O) frequency of the acyl group is in the range 1679–1692 cm^{-1} for the complexes and the five-coordinated complexes show a single band at 325–335 cm^{-1} for ν(Ir—Cl). Complex IIb when prepared in benzene solution or when recrystallized from benzene is isolated as a solvate containing $^1/_2$ mol of benzene per mole of complex. This has bands at 339 and 323 cm^{-1} in the ν(Ir—Cl) region when ir spectra of Nujol mulls are recorded. Benzene solutions show a single band at 325 cm^{-1}, as do samples dried in vacuo at 80° or recrystallized from methylene chloride. ^1H and ^{19}F NMR spectra of the $C(O)CF_nH_{3-n}$ group are similar to those of compounds Ia–c except the resonances are shifted downfield slightly (see Table II). The five-coordinated complexes IIa–c show two bands at ca. 410 and 490 nm in the visible region, each having a molar absorptivity of 300–400 M^{-1} cm^{-1} (see Table III). Solutions give linear plots of concentration vs. absorbance in the concentration range 10^{-3}–10^{-5} M. The complexes are monomeric in benzene solution (e.g., molecular weight for IIa: found, 897; calcd, 885). The molecular weights and linear Beer's law plots establish that the complexes have no tendency to dimerize in the concentration range studied.

The five-coordinated complexes II have a tendency to form crystalline solvates when isolated from benzene or methylene chloride. The benzene solvates of II have an ir band of medium intensity at 670 cm^{-1} which is absent in the spectrum of vacuum-dried samples or of samples recrystallized from methylene chloride. Bands expected to arise from vibrational modes of methylene chloride of solvation[12] in the region 700–750 cm^{-1} are apparently obscured by the strong bands arising from the out-of-plane C–H bending modes of the phenyl rings.

The five-coordinate complexes IIa–c reversibly add carbon monoxide in methylene chloride solution to give colorless complexes (eq 3). The complexes IIIa–c, in solution, have



(3)

II

III

$L = P(C_6H_5)_3$
a, $n = 3$
b, $n = 2$
c, $n = 1$

ir bands at 2064–2079 and 1652–1662 cm^{-1} (Table I) due to the terminal carbonyl and acyl groups, respectively. The addition of carbon monoxide is readily reversible as was reported for an analogous phenylacetyl complex.[6]

Methyl and Fluorine-Substituted Methyl Complexes. Complexes IIa–c undergo an alkyl group migration reaction either when refluxed in benzene or when heated in the solid state (eq 4) to a temperature characteristic of the migrating group (see Table IV for the temperatures at which the migration reaction occurs in the solid state). The temperature at which the migration occurs in the solid state is sensitive to the presence of solvent in the lattice. For example, the methylene chloride solvate and unsolvated form of the fluo-

Table IV. Analytical Results and Melting Points

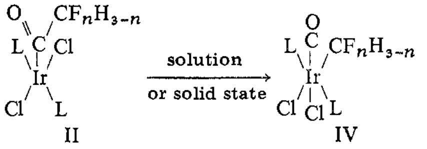
Complex[a]	Mp, °C	% C		% H		% Cl		% wt loss[c]	
		Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$IrCl_2[C(O)R](CO)L'_2$									
$R = CF_3$	210–211	44.17	43.97	3.32	3.33				
$R = CF_2H$	167–168	45.20	44.50	3.53	3.55				
$R = CFH_2$	199–201	46.28	45.58	3.74	3.56				
$IrCl_2[C(O)R]L_2$									
$R = CF_2H$									
$\cdot{}^1/_2C_6H_6$	168[b]	54.37	54.26	3.67	3.73	7.83	8.87	4.31	5.54
$\cdot{}^1/_2CH_2Cl_2$	185[b]	50.86	51.04	3.55	3.77	11.69	11.02	4.67	5.15
$R = CFH_2$	123[b]	53.78	53.59	3.80	3.75	8.35	9.81	0	0
$\cdot{}^1/_2CH_2Cl_2$	145[b]	51.89	52.39	3.73	3.75	11.93	12.23	4.76	5.80
$IrCl_2(CO)RL_2$									
$R = CF_2H$	252	52.65	52.40	3.61	3.64	8.18	8.16		
$R = CFH_2$	287	53.78	54.37	3.80	3.90	8.35	8.25		
$IrClI(CF_3)(CO)L'_2$	231–234	41.13	39.80	2.99	3.06				
$IrBrI(CF_3)(CO)L'_2$	224–226	39.15	38.19	2.84	2.85				
$IrCl_2[C(O)CF_2H][HC(O)N(CH_3)_2]L_2$[d]	100[e]	51.78	51.65	4.12	3.94				

[a] $L' = PCH_3(C_6H_5)_2$, $L = P(C_6H_5)_3$. [b] Temperature at which the five-coordinated acyl complex undergoes the migration reaction in the solid state. [c] Weight change due to loss of solvent upon heating to 150°. [d] Nitrogen analysis: calcd, 1.51; found, 1.42. [e] Solid turns orange.

Table V. Rate Constants for the Migration Reaction of Five-Coordinated Acyl Complexes, $IrCl_2[C(O)R][P(C_6H_5)_3]_2$, in Toluene

R	T,[a] °K	10^4k,[b] sec^{-1}
CFH_2	323.0	2.68
	333.0	6.45
	343.0	15.88
	353.0	44.39
CF_2H	343.0	0.45
	353.0	1.41
	363.0	3.57
CF_3	333.0	1.12
	343.0	3.03
	353.0	7.97
	363.0	20.45

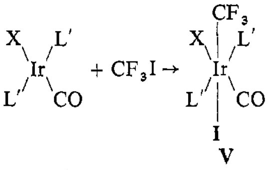
[a] Deviation ±0.1°K. [b] Standard deviation of k is 1–4%.



(4)

$L = P(C_6H_5)_3$
a, $n = 3$
b, $n = 2$
c, $n = 1$
d, $n = 0$

roacetyl complex IIc undergo the migration reaction at 145 and 123°, respectively. The same isomer of IV is obtained in the solution and solid-state reaction. Complexes IVa[6] and IVd[3] have previously been reported. Complexes IVa–d are characterized by a terminal carbonyl stretching frequency at 2085, 2078, 2060, or 2048 cm^{-1}, respectively, in the ir spectrum. In addition, each complex shows two bands in the ν(Ir–Cl) region of the ir spectra. One band in the 302–318-cm^{-1} range is assigned to ν(Ir–Cl) for chlorine trans to carbon monoxide[6,7] and the second in the range 242–273 cm^{-1} is assigned to ν(Ir–Cl) for chlorine trans to the CF_nH_{3-n} group. The infrared data for compounds IVa–d are shown in Table I. Compounds IVa and IVb each have an ir band at 281–283 cm^{-1}. It was established that this is not a metal–chlorine mode since a similar band appears in the spectra of complexes obtained by adding trifluoromethyl iodide to *trans*-chlorocarbonylbis(methyldiphenylphosphine)iridium(I) and its bromo analog (eq 5). The ir spectrum of compound Va has two bands in the 200–400-cm^{-1} region, one at 316 cm^{-1} and the other at 270 cm^{-1}. The absence of the 316-cm^{-1} band in compound Vb identifies it as ν(Ir–Cl) for Cl trans to CO. The 270-cm^{-1} band is present in both Va and Vb; hence it is not an iridium–chlorine mode. This band may correspond to that near 300 cm^{-1} mentioned by Clark et al. in their study of trifluoromethylplatinum complexes. They suggested it may involve some ν(M–C) character.[13]



(5)

$L' = PCH_3(C_6H_5)_2$
a, X = Cl
b, X = Br

Attempts to add trifluoromethyl chloride oxidatively to *trans*-$IrCl(CO)[PCH_3(C_6H_5)_2]$ gave only very slight conversion to the six-coordinate adduct, ν(C≡O) at 2084 cm^{-1}, after 3 days of reaction at room temperature in benzene at 40 psi.

Migration Reaction Kinetics. Kinetic measurements for the migration reaction of compounds IIa–c (eq 4) in toluene solution were made by following the decay of the absorption band at ca. 410 nm. Kinetic parameters are given in Tables V and VI. It was not possible to study the reaction in more polar solvents such as dimethylformamide. In this solvent solutions of IIa–c are colorless. This corresponds to occupation of the vacant coordination site by a solvent molecule (eq 6).

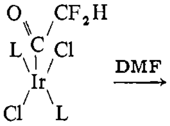
Table VI. Activation Parameters for the Migration of CF_nH_{3-n} Groups

R	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J K^{-1} mol^{-1}
CFH_2	85.5 ± 1.4	−49.8 ± 6
CF_2H	104.4 ± 1.4	−24.7 ± 2
CF_3	94.4 ± 0.2	−38.1 ± 1

Table VII. Differential Scanning Calorimeter Data for the Migration Reaction in Five-Coordinated Acyl Complexes, $IrCl_2[C(O)R][P(C_6H_5)_3]_2\cdot{}^1/_2CH_2Cl_2$[a]

R	T_i, °K	T_p, °K	T_f, °K	ΔH_0, kJ mol^{-1}
CFH_2	410	418	424	−46 ± 5
CF_2H	447	459	464	−66 ± 8
CF_3	425	445	453	−84 ± 4
CH_3				−27 ± 5[b]

[a] For R = CF_3 the complex is isolated in the unsolvated form. [b] ΔH_0 estimated by extrapolation from data for the fluoromethyl groups.



$\xrightarrow{DMF} IrCl_2[C(O)CF_2H]L_2[H(O)CN(CH_3)_2]$ VI (6)

A pale yellow crystalline compound, VI, was isolated from the solution. Analytical and ir data are consistent with the formation of a 1:1 adduct. The ν(C═O) region shows bands at 1645, 1634, and 1619 cm^{-1}. The shift of ν(C═O) of the difluoroacetyl group from 1681 cm^{-1} to a lower frequency is consistent with coordination of a ligand trans to the acyl group.[6]

Thermochemical Measurements. The enthalpy change, ΔH_0, for the migration reaction of compounds IIb and IIc in the solid state was determined by differential scanning calorimetry. The value of ΔH_0 for the migration of the trifluoromethyl group in compound IIa has been reported in an earlier communication.[5] Table VII summarizes the data obtained for the three compounds. The enthalpy change for the migration reaction has been shown to be independent of temperature in the range 273–460°K for R = p-$O_2NC_6H_4CH_2$ and CF_3.[5]

The five-coordinated complex IId containing the unsubstituted acetyl group could not be isolated; hence no value for the enthalpy change was measured. An approximate value can be obtained by an extrapolation of the data for the fluorine-substituted derivatives. As is shown in Figure 1 a plot of the enthalpy change for the migration of the CF_nH_{3-n} group vs. the number of fluorines, n, is linear. Extrapolation to n = 0 yields a value of approximately 27 ± 5 kJ mol^{-1} for the enthalpy change for the migration of the methyl group.

Discussion

A series of five-coordinated acyl complexes $IrCl_2[C(O)CF_nH_{3-n}][P(C_6H_5)_3]_2$ (compounds IIa–c) has been synthesized as part of a detailed kinetic and thermochemical study of migration reactions of acyl complexes of transition metals. Fluorine-substituted acetyl complexes were chosen since the fluorinated methyl group undergoes the migration reaction shown in eq 4 at a rate which allows isolation of the five-coordinated complex and the series gives a wide variation of the electronegativity of the alkyl group attached to the acyl carbon. In order to evaluate the effect on the physical properties of increasing substitution by fluorine at the methyl carbon in the acetyl complexes or in complexes in which the methyl group is directly bonded to the iridium the complete series of six-coordinate acyl complexes having the formula

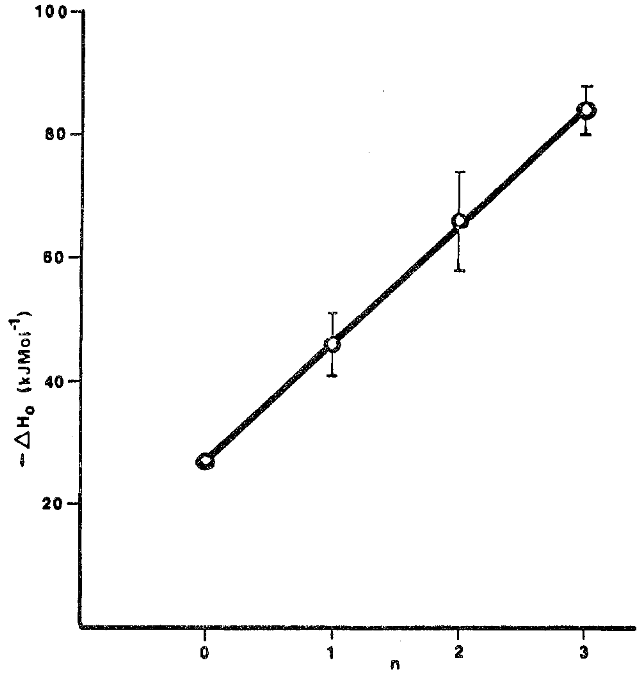
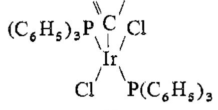


Figure 1. Extrapolation of the enthalpy change for the migration of substituted methyl groups, CF_nH_{3-n}, as a function of the number of fluorines, n, to $n = 0$.

$IrCl_2[C(O)CF_nH_{3-n}](CO)[PCH_3(C_6H_5)_2]_2$, compounds Ia–d, and the substituted-methyl complexes $IrCl_2(CF_nH_{3-n})(CO)[P(C_6H_5)_3]_2$, compounds IVa–d, were prepared.

The trans influence of the substituted acetyl groups can be inferred from the iridium–chlorine stretching frequency for the chlorine trans to $C(O)CF_nH_{3-n}$ in compounds Ia–d. The trans influence decreases in the series $C(O)CH_3 > C(O)CH_2F > C(O)CHF_2 > C(O)CF_3$. The values of ν(Ir–Cl) range from 238 to 260 cm^{-1} in the series. The trans influence of the CF_nH_{3-n} group assessed from the iridium–chlorine stretching frequencies in compounds IVa–d decreases in the series $CH_3 > CHF_2 \approx CH_2F > CF_3$. The range of values is larger, 242–273 cm^{-1}, than that observed in the corresponding acetyl derivatives. The trans influence as measured by ν(Ir–Cl) is more sensitive to substitution at the ligating atom as suggested by Dent et al.[14] but is only slightly attenuated by the intervening carbon atom in the acyl complexes. The trans influences of acyl groups on a trans carbonyl group in compounds IIIa–c show a trend differing from that measured by ν(Ir—Cl). ν(C≡O) decreases in the order $CF_2H > CF_3 > CH_2F$.

The five-coordinated complexes IIa–c are models for coordinatively unsaturated intermediates in migration reactions in acyl complexes.[1,15] The complexes $IrCl_2[C(O)R][P(C_6H_5)_3]_2$ (R = CF_3, CF_2H, CFH_2) and those previously reported by Kubota, Blake, and Smith[2] (R = CH_2Y, where Y = p-$NO_2C_6H_4$, p-$CH_3C_6H_4$, p-$CH_3OC_6H_4$, or C_6H_5) are probably square pyramidal, with the acyl group at the apex.



II

This is in accord with Pearson's prediction that five-coordinate d^6 complexes should favor a square-pyramidal geometry.[16] A rhodium(III) complex, $RhI_2(CH_3)[P(C_6H_5)_3]_2$, has been found to have this structure.[17] The presence of a single ν(Ir–Cl) band in the complexes at 325–335 cm^{-1} lends support to this assignment of structure to compounds IIa–c.

The enthalpy changes, ΔH_0, for the migration reaction of the five-coordinate acyl complexes in the solid state (eq 4) become less exothermic in the series CF_3 (−84 ± 4 kJ mol^{-1}) > CF_2H (−66 ± 8 kJ mol^{-1}) > CFH_2 (−46 ± 5 kJ mol^{-1}) > CH_3 (∼−27 ± 5 kJ mol^{-1}). Values previously reported for substituted benzyl groups averaged −15 kJ mol^{-1}.[5] The heat of reaction in solution is related to that measured in the solid state by eq 7 where $\Delta H_{\mathrm{solv}_6}$ and $\Delta H_{\mathrm{solv}_5}$ are the heat of solution

$$\Delta H_{\mathrm{soln}} = \Delta H_{0\mathrm{s}} + \Delta H_{\mathrm{solv}_6} - \Delta H_{\mathrm{solv}_5} \qquad (7)$$

of the six- and five-coordinated compounds, respectively. These heats of solution are expected to be small and similar in magnitude for nonpolar solvents. Therefore the measured values of the enthalpy change in the solid state should be a good approximation of the value in solution. The heat of reaction will primarily be determined by the bond energy terms given in eq 8 (n = 0, 1, 2, or 3; hydrogens are omitted for

$$\begin{aligned}\Delta H_0 = {} & E[\mathrm{C(O)}{-}\mathrm{CF}_n] + E[\mathrm{Ir}{-}\mathrm{C(O)CF}_n] + E(\mathrm{C}{=}\mathrm{O}) - {}\\ & [E(\mathrm{Ir}{-}\mathrm{CF}_n) + E(\mathrm{Ir}{-}\mathrm{CO}) + E(\mathrm{C}{\equiv}\mathrm{O})] \qquad (8)\end{aligned}$$

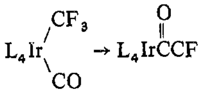
clarity). If reasonable assumptions[18–20] are made about the constancy of bond energies for those bonds separated by two or more bonds from the substituents in the methyl group, then eq 8 reduces to eq 9. If the first term, $E[\mathrm{C(O)}{-}\mathrm{CF}_n]$, remains

$$\Delta H_0 = E[\mathrm{C(O)}{-}\mathrm{CF}_n] - E(\mathrm{Ir}{-}\mathrm{CF}_n) + \text{constant} \qquad (9)$$

constant or increases with increasing substitution as is suggested by the limited information available concerning the effect of fluorine substitution on the bond energy of adjacent carbon–carbon bonds,[18–20] then the slope of the graph in Figure 1 becomes a lower limit on the incremental increase of the iridium–carbon bond energy as hydrogen is replaced by fluorine in the methyl group. This number is about 20 kJ mol^{-1} per fluorine. This leads to the suggestion that the Ir–CF_3 bond may be at least 57 ± 9 kJ mol^{-1} stronger than the Ir–CH_3 bond, which supports the current belief in a stronger metal–carbon bond in fluorocarbon complexes compared to in the hydrocarbon analogs.[13] Since no transition metal–fluorocarbon bond energies have been determined this estimate cannot be substantiated at present.

The kinetics of the migration reaction have been studied in toluene solution in the temperature range 323–363°K. These data are shown in Tables V and VI. The reactions are slow which is consistent with the observation that in the migration of substituted benzyl groups (p-$XC_6H_4CH_2$) the rate of migration decreases as the electronegativity of the substituent increases.[2,4] Surprisingly, the rate decreases in the order $CFH_2 > CF_3 > CF_2H$ rather than in the expected order of increasing electronegativity. The only parameter found to correlate with this trend is the electron-withdrawing property of the acyl group indicated by ν(C≡O) in compounds IIIa–c where carbon monoxide is trans to the $C(O)CF_nH_{3-n}$ group. In these compounds ν(C≡O) shows a modest increase that parallels the decreasing migration rate. With this taken as the indicator of the group electronegativity it can be seen that $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ both increase (become more positive) with increasing electronegativity in $C(O)CF_nH_{3-n}$. This is the same trend observed in the migration of substituted benzyl groups.[2] The lack of correlation between ΔH_0 and $\Delta H^{\ddagger}$ for the compounds may indicate that the transition state is more like the starting complex than the product.

The reverse of the migration reaction, i.e., the insertion of carbon monoxide into a transition metal–fluorocarbon bond, has not been accomplished.[1] The reason can be either kinetic or thermodynamic in origin. From the kinetic and thermochemical data reported here it is possible to obtain an approximate value for the enthalpy of activation for the insertion of carbon monoxide into an iridium–fluorocarbon bond (eq 10). If it is assumed that this is the reverse of eq 4, then the



$$L_4Ir(CF_3)(CO) \rightarrow L_4IrC(O)CF_3 \qquad (10)$$

activation enthalpy, $\Delta H_{10}^{\ddagger}$, will be given by eq 11. The value

$$\Delta H_{10}^{\ddagger} = \Delta H_4^{\ddagger} - \Delta H_0 \qquad (11)$$

of $\Delta H_{10}^{\ddagger}$ would be about +178 ± 5 kJ mol^{-1} for the CF_3 group; hence carbon monoxide insertion would be a very slow reaction. This is consistent with the observation that insertion in alkylmanganese complexes is slower for CFH_2 than CH_3 and not observed for CF_3.[21] Overall, the insertion reaction would probably be thermodynamically favorable since in the presence of excess carbon monoxide the coordinatively unsaturated product of reaction 10 would add carbon monoxide as a sixth ligand, gaining the M–CO bond energy (ca. 120–170 kJ mol^{-1})[22] which would offset the endothermic contribution from the insertion step.

Experimental Section

The complexes $IrX(CO)[PCH_3(C_6H_5)_2]_2$ (X = Cl or Br)[7] and $IrCl(N_2)[P(C_6H_5)_3]_2$[23] were prepared using published procedures. Trifluoroacetyl chloride, trifluoromethyl iodide, and difluoroacetic acid were purchased from PCR, Inc., and monofluoroacetic acid was purchased from Pfaltz and Bauer, Inc. Benzene used in the syntheses was doubly distilled and stored in vacuo. Infrared spectra were recorded on a Perkin-Elmer Model 621 spectrometer; proton and fluorine NMR spectra were obtained on Varian T-60 and HA-100 spectrometers using deuteriochloroform as a solvent. Electronic spectra were recorded on a Cary 14. Molecular weights were determined on a Mechrolab osmometer. Melting points were determined on a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Mono- and Difluoroacetyl Chloride. The acyl halides were prepared from the corresponding acids by reaction with benzoyl chloride (monofluoro) or phosphoryl chloride (difluoro).[24] Samples were stored in vacuo in containers with Teflon stopcocks. Infrared spectra showed the samples to be free of hydrogen chloride and the chlorinating reagent. Monofluoroacetyl chloride: NMR (CD_2Cl_2) τ 4.95 (d, J(H–F) = 52 Hz); vapor pressure (23°) 105 Torr. Difluoroacetyl chloride: NMR (CD_2Cl_2) τ 5.97 (t, J(H–F) = 54 Hz); vapor pressure (27°) 640 Torr.

$IrCl_2[C(O)CF_nH_{3-n}](CO)[PCH_3(C_6H_5)_2]_2$ (n = 0, 1, 2, or 3). Benzene, 3 ml, and the appropriate substituted acetyl chloride, 0.2 ml, were condensed onto 0.35 g of *trans*-chlorocarbonylbis(methyldiphenylphosphine)iridium(I) at −176° in vacuo. The mixture was allowed to warm to room temperature and stir for 10 min. The volatile components of the mixture were removed in vacuo. Subsequent operations were carried out without exclusion of air. The glassy residue was triturated with 15 ml of diethyl ether to give the colorless crystalline product in nearly quantitative yield. The product thus isolated was sufficiently pure for most purposes but the complexes are readily recrystallized from benzene–n-hexane.

$IrCl_2[C(O)CF_2H][P(C_6H_5)_3]_2$. Toluene, 5 ml, and difluoroacetyl chloride, 0.15 ml, were condensed onto 0.4 g of *trans*-chlorodinitrogenbis(triphenylphosphine)iridium(I) at −176° in vacuo. The mixture was warmed to 0° and allowed to stir for 15 min. Subsequent operations were carried out with no precautions to exclude air. The orange suspension was filtered to give the light orange product in 85% yield. The crude product may be conveniently recrystallized from either benzene–n-hexane or methylene chloride–diethyl ether. In each case it is isolated as a solvate containing $^1/_2$ mol of benzene or methylene chloride, respectively. Molecular weight (C_6H_6): found (for methylene chloride solvate), 897; calcd, 909.

$IrCl_2[C(O)CFH_2][P(C_6H_5)_3]_2$. Benzene, 4 ml, and monofluoroacetyl chloride, 0.2 ml, were condensed onto 0.5 g of the dinitrogen complex at −176° in vacuo. The mixture was warmed to room temperature and stirred for 8–10 min. Subsequent work-up was done open to the air. Filtration of the orange suspension gave the product in 80% yield. Recrystallization of the crude product from hot benzene–n-hexane results in some conversion (ca. 5–10%) to the six-coordinated carbonyl complex. Recrystallization from methylene–chloride yields a product which contains $^1/_2$ mol of CH_2Cl_2 of solvation. Molecular weight (C_6H_6): found, (methylene chloride solvate), 907; calcd, 891.

$IrCl_2[C(O)CF_3][P(C_6H_5)_3]_2$. Recrystallization of a sample of complex prepared as previously reported[3] from methylene chloride–diethyl ether gave orange needles which contained less than 0.1 mol of solvent. Molecular weight (C_6H_6): found, 897; calcd, 885.

$IrCl_2(CF_nH_{3-n})(CO)[P(C_6H_5)_3]_2$ (n = 1, 2, or 3). Procedure A. A 0.15-g sample of the corresponding five-coordinated acyl complex was heated at 150–175° in vacuo for 10 min. During this time the orange color faded to nearly colorless. A quantitative yield of analytically and spectroscopically pure product was obtained.

Procedure B. A 0.15-g sample of the corresponding five-coordinated acyl complex was refluxed in benzene, 5 ml, for 24 hr. The nearly colorless mixture was cooled to room temperature and filtered yielding the product in ca. 60–70% yield.

Samples prepared by the two methods were identical.

$IrIX(CF_3)(CO)[PCH_3(C_6H_5)]_2$ (X = Cl or Br). Benzene, 5 ml, and trifluoromethyl iodide, 0.1 ml, were condensed onto 0.4 g of *trans*-$\{IrX(CO)[PCH_3(C_6H_5)_2]_2\}$ at −176° in vacuo. The mixture was warmed to room temperature and stirred for 24 hr. The clear yellow solution was evaporated to dryness on a rotary evaporator. Diethyl ether, 15 ml, was added to the sticky residue, resulting in the formation of a light yellow precipitate. The yield in each case was 80%. The product was recrystallized from benzene–n-hexane. X = Br: NMR ($CDCl_3$) τ 7.28 (t, $J(PCH_3)$ = 10 Hz). X = Cl: NMR ($CDCl_3$) τ 7.38 (t, $J(PCH_3)$ = 10 Hz).

$IrCl_2[C(O)CF_2H][P(C_6H_5)_3]_2[(CH_3)_2NC(O)H]$. To 2 ml of dimethylformamide was added 0.08 g of the coordinatively unsaturated acyl complex, IIb. The colorless solution was stirred and 5 ml of diethyl ether was added. Refrigeration for 3 hr resulted in the formation of pale yellow needles (yield 90%).

Kinetic Measurements. The extent of reaction was monitored spectrophotometrically using a Cary 14 recording spectrophotometer using 1-cm water-jacketed cells. Initial concentrations were in the range 2×10^{-3}–5×10^{-4} M. The band at ca. 410 nm was used to follow the reaction. Plots of log $(A - A_\infty)$ as a function of time were linear for 4 half-lives for the trifluoroacetyl complex, IIa. In the cases of the difluoro- and monofluoroacetyl complexes, IIb and IIc, the six-coordinated products $IrCl_2CF_nH_{3-n}(CO)L_2$ undergo a slow reaction subsequent to their formation in the migration step. The product of this reaction absorbs at 410 nm which led to slight curvature in the ln $(A - A_\infty)$ plots after the first half-life. Therefore, the first-order rate constants for the migration step for compounds IIb and IIc were evaluated for the first half-life where the decomposition rate was not yet significant. The values of A_∞ in these two cases were obtained using freshly prepared solutions of authentic samples of the six-coordinated products.

Differential Scanning Calorimetry. A Perkin-Elmer differential scanning calorimeter, DSC-1B, was used to measure the enthalpy change ΔH_T for the alkyl group migration of the acyl complexes. The instrument was connected to a pen recorder (Leeds & Northrup). The enthalpy change was proportional to the peak area traced by the pen. Indium metal (Fisher Scientific, 99.99%) with mp 429°K and heat of fusion 0.78 kcal/mol was used to calibrate the instrument in the upper temperature range 273–773°K. The sensitivity range settings of 2, 4, and 8 mcal (full scale deflection)$^{-1}$ sec^{-1} were used with temperature scanning rate at +10° min^{-1} and recorder chart speed of 1 in. min^{-1}. An electromicrobalance (Cahn Instrument, 0.001-mg resolution) was used to weigh out the sample (2–6 mg) which was contained in a small pan (Perkin-Elmer) made of an aluminum sheet of 0.0055-in. thickness. A lid of the same material was placed on top of the sample inside the pan. The sample was then pressed in the pan by a hand crimper. The crimped sample was placed on the sample holder of the instrument and an empty aluminum pan was placed on the reference holder. At least ten independent determinations of ΔH_T were made for each compound.

Acknowledgment. Acknowledgment is made to The Robert A. Welch Foundation for support of this work and for a graduate fellowship (Y.L.C.) and an undergraduate fellowship (A.W.). We thank Dr. Dennis Deavenport for obtaining the ^{19}F spectra.

Registry No. Ia, 54667-51-5; Ib, 54657-58-8; Ic, 54657-59-9; Id, 20313-03-5; IIa, 54676-79-8; IIb, 54657-60-2; IIc, 54657-61-3; IId, 54657-62-4; IIIa, 54676-80-1; IIIb, 54657-63-5; IIIc, 54657-64-6; IVa, 51293-22-2; IVb, 42126-59-0; IVc, 54657-65-7; IVd, 33394-14-8; Va, 54676-81-2; Vb, 54657-66-8; VI, 54657-67-9; *trans*-chlorocarbonylbis(methyldiphenylphosphine)iridium(I), 15318-32-8;

trans-chlorodinitrogenbis(triphenylphosphine)iridium(I), 21414-18-6; *trans*-bromocarbonylbis(methyldiphenylphosphine)iridium(I), 19354-07-5; trifluoroacetyl chloride, 354-32-5; difluoroacetyl chloride, 381-72-6; monofluoroacetyl chloride, 359-06-8; acetyl chloride, 75-36-5; trifluoromethyl iodide, 2314-97-8.

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Trans-Ligand Effects in the Insertion Reactions of Ethylene and Phenylmethylacetylene with Neutral and Cationic Hydridoplatinum(II) Complexes

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A series of cationic *trans*-$(PEt_3)_2PtHL^+PF_6^-$ (L = acetone, CO, PEt_3, $AsPh_3$, $P(OMe)_3$, $P(OPh)_3$) and neutral *trans*-$(PEt_3)_2PtHX$ (X^- = Cl^-, NO_3^-, NO_2^-, CN^-) complexes has been prepared and allowed to react with ethylene and phenylmethylacetylene. The reactivity to give inserted products is found to be a function of the trans group, L or X^-. Although the acetylene is the more reactive toward insertion, the same order of reactivity is found for both ethylene and phenylmethylacetylene. Reactivity of the cationic hydrides decreases in the order L = acetone >> CO > $AsPh_3$ > $P(OPh)_3$, $P(OMe)_3$, PEt_3 while the neutral hydrides follow the order X^- = NO_3^- > Cl^-, NO_2^-, CN^-. The mechanistic implications are considered and a general mechanism for insertion is proposed.

Chatt and Shaw's[1] initial demonstration of the insertion reaction 1 has provided a mechanistic foundation for many

$$\underset{\text{I}}{trans\text{-}(PEt_3)_2PtHCl} + C_2H_4 \xrightarrow[40\ \text{atm}]{90°} \underset{\text{II}}{trans\text{-}(PEt_3)_2PtC_2H_5Cl} \qquad (1)$$

discussions of homogeneous catalytic hydrogenation and isomerization.[2,3]

The intimate details of reaction 1 were initially assumed[4,5] to involve associative olefin coordination to give a five-coordinate hydridoolefin intermediate, followed by a migratory rearrangement and collapse to a square-planar insertion product. It has been pointed out that, in certain cases, an alternative mechanistic pathway not previously considered may apply.[6]

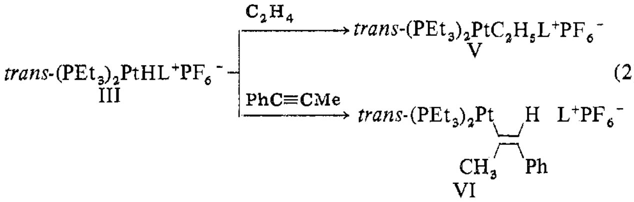
Thus, when the ligand trans to hydride is very weakly coordinating (e.g., as with acetone or NO_3^- [7]), a mechanism involving olefin coordination in the nascent site with displacement of the trans ligand to give a four-coordinate hydridoolefin complex is operative.

We recently presented evidence regarding this apparent mechanistic dichotomy[8] and discussed kinetic data which establish that in certain cases insertion proceeds by the latter mechanism.[9,10]

Some additional results reported herein indicate that the insertion of olefins and acetylenes into platinum–hydrogen bonds of square-planar Pt(II) complexes may be more profitably described in terms of a unified reaction scheme wherein the fate of the initially formed five-coordinate species is determined in large part by the ligand trans to hydride. Hence, the reaction may lead to insertion directly or to insertion via a pathway involving preliminary substitution.

Results

In an attempt to determine the mechanistic significance of the trans ligand we have investigated reactions 2 and 3 using a number of neutral (L) or anionic (X^-) groups.



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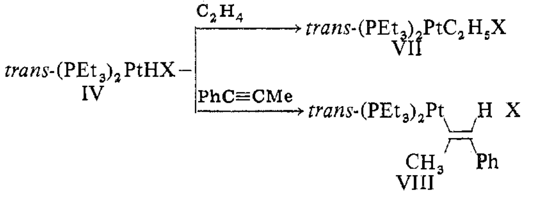

(3)

Reactions with Ethylene. Since the reaction of platinum(II) hydride complexes with nonterminal, fluorine- or cyano-substituted olefins is complicated by low yields of alkyl product[6] or competition from reactions other than insertion,[11,12] we have chosen ethylene as a model olefinic substrate. Samples containing the hydride complexes III or IV in acetone solution were prepared and sealed in NMR tubes with 1.5 equiv of ethylene. The tubes were placed in a thermostated bath at 35° and monitored by observing changes in the upfield NMR signal due to Pt–H. After 6 months the tubes were opened and the contents analyzed by examination of their infrared spectra.