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NEW COORDINATIVELY UNSATURATED ACYLIRIDIUM(III) COMPOUNDS INCLUDING A NEW PYRUVOYL COMPLEX. SYNTHESIS, KINETICS AND THERMOCHEMISTRY

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Summary

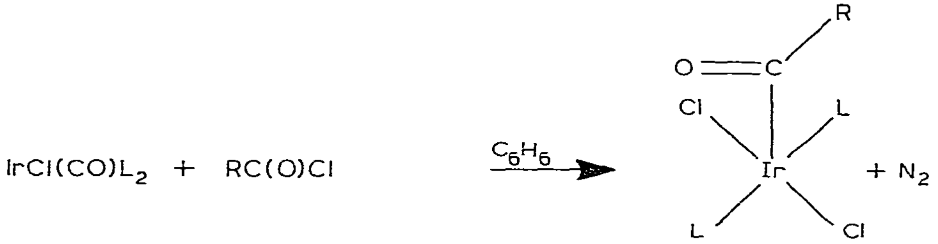
The reaction of acyl chlorides with *trans*-$[\mathrm{IrCl(N_2)(PPh_3)_2}]$ has been used to prepare new examples of coordinatively unsaturated acyliridum(III) complexes, $\{\mathrm{IrCl_2[C(O)R](PPh_3)_2}\}$ (R = $\mathrm{CH_2Cl}$, $\mathrm{CH_2OPh}$, C(O)OEt, $\mathrm{CH_2CH_2C(O)OMe}$ or $\mathrm{C(O)CH_3}$). In the case of ethyl malonyl chloride a chelated complex is obtained: $\{\overline{\mathrm{IrCl_2[C(O)CH_2C(O}}\mathrm{)OEt](PPh_3)_2}\}$. All of these complexes undergo a spontaneous migration reaction to give the coordinatively saturated product $[\mathrm{IrCl_2R(CO)(PPh_3)_2}]$. The coordinatively unsaturated pyruvoyl complex behaves atypically. Exposure of the solid to light yields the acetyl complex, $\{\mathrm{IrCl_2[C(O)CH_3](CO)(PPh_3)_2}\}$, while heating the solid in the dark yields the methyl complex, $[\mathrm{IrCl_2(CH_3)(CO)(PPh_3)_2}]$. A coordinatively saturated pyruvoyl complex is obtained by addition of pyruvoyl chloride to Vaska's complex. The rates of migration of $\mathrm{CH_2Cl}$, $\mathrm{CH_2OPh}$ and C(O)OEt were determined in ethylene dichloride solution and the ground state enthalpy change for the migration of these groups was obtained by differential scanning calorimetry as was that for conversion of $\{\mathrm{IrCl_2[C(O)C(O)CH_3](PPh_3)_2}\}$ to $[\mathrm{IrCl_2(CH_3)(CO)(PPh_3)_2}]$ + CO.

Introduction

Five-coordinated acyl complexes of metal ions with a d^6 configuration have been implicated as intermediates in carbon monoxide insertion reactions and decarbonylation reactions in numerous catalytic and stoichiometric systems [1—3]. Because they are coordinatively unsaturated such species normally cannot be isolated and often cannot be detected. We have used a method previously discovered by us [4,5] to prepare new examples of coordinatively unsaturated acyliridium(III) compounds for kinetic, spectroscopic and thermochemical study. Of particular interest are compounds having sp^2 hybridized substituents in the α-position of the acyl group since little quantitative information is available concerning migration of —C(=O)R′ groups which are possibly involved in the Fischer—Tropsch reaction [6].

Results

New five-coordinated acyliridium(III) complexes were prepared by the oxidative addition of acyl chlorides to *trans*-$[IrCl(N_2)(PPh_3)_2]$ (eq. 1, $L = PPh_3$).



(1)

(Ia , CH_2Cl ;
Ib , CH_2OPh ;
Ic , C(O)OEt ;
Id , $CH_2CH_2C(O)OMe$
Ie , $C(O)CH_3$)

The reaction is accompanied by evolution of dinitrogen and formation of a dark orange color characteristic of the five-coordinated acyl species [4,5]. In each case it was possible to isolate the coordinatively unsaturated complexes Ia—Ie as crystalline solids. Because they spontaneously undergo the migration reaction they could not be recrystallized. These are characterized by a strong IR band at ca. 1630—1690 cm^{-1} (Table 1) characteristic of the MC(=O)R group and a band of medium intensity at 330—340 cm^{-1} assigned to ν(Ir—Cl) (see Table 1) [4,5]. The α- or γ-keto or carboxy acyls, Ic—Ie, also have a band at ca. 1720 cm^{-1} assigned to ν(C=O) of the keto or ester group [7]. The five-coordinated complexes are in general characterized by two bands in the visible region of the spectrum at ca. 400 and 470 nm. The pyruvoyl complex absorbs very strongly in the near UV and only a weak shoulder is evident at 470 nm. These spectral features are typical of those found in other coordinatively unsaturated acyliridium(III) which we have studied [4,5].

Di- and tri-chloroacetyl chloride both react rapidly with the dinitrogen complex but the materials recovered from the reaction mixture show no bands in the C=O or C≡O region of the IR and were not characterized further. Similar behavior has been reported in the case of additions of chloro-substituted acetyl chlorides with Vaska's complex [8].

In the case of ethyl malonyl chloride the orange color of the five-coordinated acyl product was momentarily observed in the reaction mixture but a light yellow product rapidly precipitated from the solution. Infrared spectra of the solid showed only a single band characteristic of ν(C=O) at 1544 cm^{-1} but

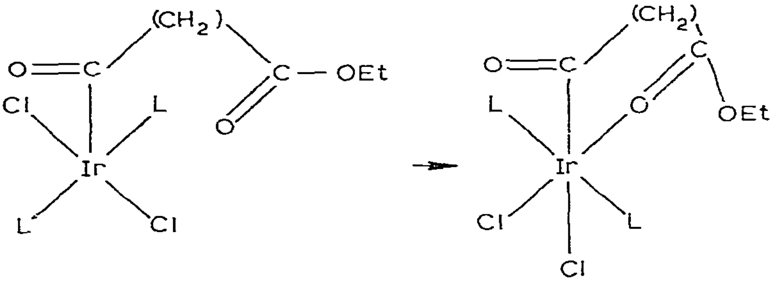
TABLE 1

INFRARED (cm^{-1}) AND VISIBLE SPECTROSCOPY DATA

	$\nu(C{\equiv}O)$ [a]	$\nu(C{=}O)$ [a]	$\nu(Ir\text{-}Cl)$ [a]	Other	Vis [b]	
					nm	ε
$IrCl_2[C(O)R]L_2$						
R = C(O)OEt		1725(s) 1668(s)	320	1230(s)	410 475	428 297
R = $C(O)CH_3$		1716(s) 1637(s)	339, 326 312		470(sh)	
R = CH_2Cl		1695(s)	322		410 487	253 330
R = CH_2OPh		1684(s)	323		395 470	509 315
R = $CH_2C(O)OEt$		1544(s)	319, 268	1360(m), 1335(s) 1195(s), 780(m)		
R = $CH_2CH_2C(O)OMe$		1746(s) 1678(s)	320	1230		
$IrCl_2R(CO)L_2$						
R = C(O)OEt	2074	1608	315			
R = CH_2Cl	2053		310 269			
R = CH_2OPh	2060	1601	304 285			
R = $CH_2C(O)OEt$	2050	1712	305 260	1240(m)		
R = $CH_2CH_2C(O)OMe$	2042	1740				
R = CH_3 [c]	2045					
R = $C(O)CH_3$ [c]	2065	1520				
$\{IrCl_2[C(O)C(O)CH_3]\text{-}(CO)(PPh_3)_2\}$	2036	1706 1650			440 385(sh)	60

[a] Nujol mull. [b] 1,2-$C_2H_4Cl_2$ solution. [c] CH_2Cl_2; Ref. 4a.

no band was observed in the ester $\nu(C{=}O)$ region. This and the lack of absorption maxima in the visible region suggest that a six-coordinated complex having a chelated structure was produced (eq. 2). New bands assigned to the coordinated ester group are found at 1360(m), 1335(s) and 1195(s) cm^{-1} and 319 and 268 cm^{-1} bands are found in the $\nu(Ir{-}Cl)$ region, consistent with the geometry shown with one Ir—Cl bond *trans* to an oxygen donor and one *trans* to a σ-bonded carbon donor. The very large shifts in the positions of $\nu(C{=}O)$ of

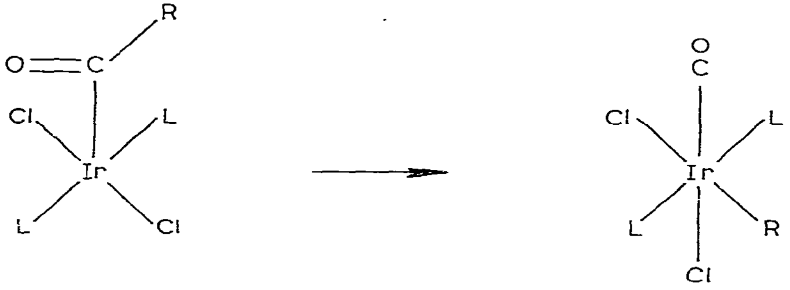


(2)

(II)

the acyl and ester groups are surprising [9]; however, additional support for the structures comes from conversion of the compound, upon reflux in benzene, to the complex $\{IrCl_2[CH_2C(O)OEt](CO)(PPh_3)_2\}$ whose characterization is discussed later.

The coordinatively unsaturated acyl complexes Ia—Ie and complex II spontaneously undergo a migration reaction, either as solids (except II) at elevated temperatures or in solution (eq. 3). All of the products show a strong $\nu(C\equiv O)$



(3)

(III)

band in the region 2040—2075 cm^{-1}. The geometry of the six-coordinated products can be unambiguously assigned based on the two bands in the $\nu(Ir—Cl)$ region characteristic of Cl *trans* to CO and of Cl *trans* to an alkyl group [4,5]. In addition, bands characteristic of $\nu(C=O)$ in the R group are observed in the IR when R = C(O)OEt, $C(=O)CH_3$ or $(CH_2)_nC(=O)OCH_3$. The esters also show the characteristic $\nu(C—O)$ at 1235 cm^{-1} [7]. This indicates that in the case of the malonyl group migration produces the carbon-bonded form of the $CH_2C(=O)OEt$ group as the isolable product rather than the O-bonded enolate anion. The possibility of formation of the O-bonded form as an intermediate in the process cannot be excluded by the data available to us.

For some of the coordinatively unsaturated complexes which undergo the migration reaction quantitatively in the solid state (R = CH_2Cl, CH_2OPh or C(O)OEt), ΔH for the rearrangement process has been determined. Differential scanning calorimetric (DSC) methods which we have previously discussed [5], were used. These data are presented in Table 2. The transitions are well

TABLE 2

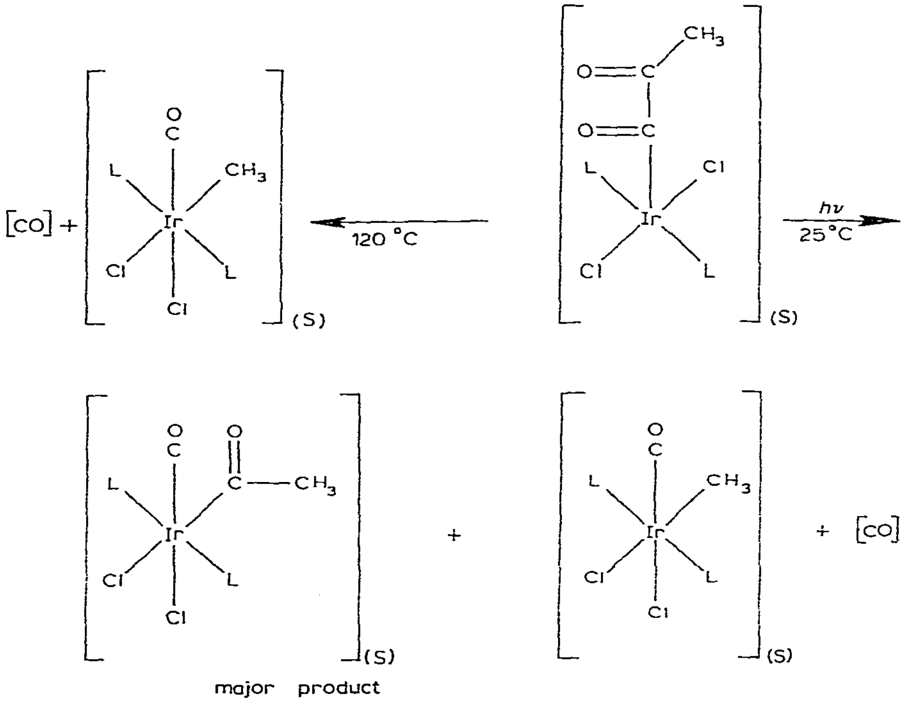
DIFFERENTIAL SCANNING CALORIMETRY DATA FOR MIGRATION REACTIONS OF $\{IrCl_2[C(O)R](PPh_3)_2\}$ IN THE SOLID STATE

R	T_i(K)	T_p(K)	T_f(K)	ΔH [a] (kcal mol^{-1})
CH_2Cl	380	405, 418	441	—14.1 ± 0.6
CH_2OPh	376	386	395	—7.5 ± 0.6 [c]
	400	408	418	
C(O)OEt	376	401	423	—10.9 ± 0.4
$C(O)CH_3$ [b]	370	397	406	—8.9 ± 0.3

[a] Each ΔH is the mean of at least six determinations. Error limits are one standard deviation. [b] The products are $[IrCl_2CH_3(CO)(PPh_3)_2]$ and CO. [c] The total ΔH is given. Values for the two partial transitions are —3.3 ± 0.3 and —4.2 ± 0.3 kcal/mol, respectively.

separated from the melting points of the products. For the monochloromethyl and phenoxymethyl migrating groups two maxima were observed in the DSC experiment in the temperature region corresponding to the migration of the R group. The peaks are not separated for the chloro compound but are for the phenoxy complex. This behavior is possibly due to the presence of two crystalline forms or rotational [10] isomers of $IrC(=O)CH_2X$ in the sample. Support for the presence of forms migrating at different temperatures is provided by infrared spectra run on samples of $\{IrCl_2[C(O)CH_2OPh](PPh_3)_2\}$ after heating to 398 K, a temperature which is between the two maxima. At that point $\nu(C{\equiv}O)$ of migrated product and $\nu(C{=}O)$ characteristic of five-coordinated complex are both observed. We have used the total heat change for the two transitions as the enthalpy of migration in these cases. The ethyl oxalyl complex shows a single maximum at 401 K with a ΔH of -10.9 ± 0.4 kcal mol^{-1}. Kinetic data have been obtained for the same reactions in solution. In each case, the reaction is first-order in five-coordinated complex and plots of $\ln(A - A_\infty)$ vs. time are linear for at least 4 half-lives. These data are given in Table 3.

The reactions of the coordinatively unsaturated pyruvoyl complex, Ie, are not typical of those found for other acyliridium complexes reported here and in previous work. The coordinatively unsaturated complex is very light-sensitive. Exposure of the orange solid to room light or sunlight causes it to be converted to a colorless solid which was shown by its IR spectrum to be a mixture of predominantly the acetylcarbonyl complex, which would be expected, and some of the methylcarbonyl complex formed by elimination of carbon monoxide (approximately an 80/20 mixture) (eq. 4). Surprisingly, heating the solid



(4)

TABLE 3

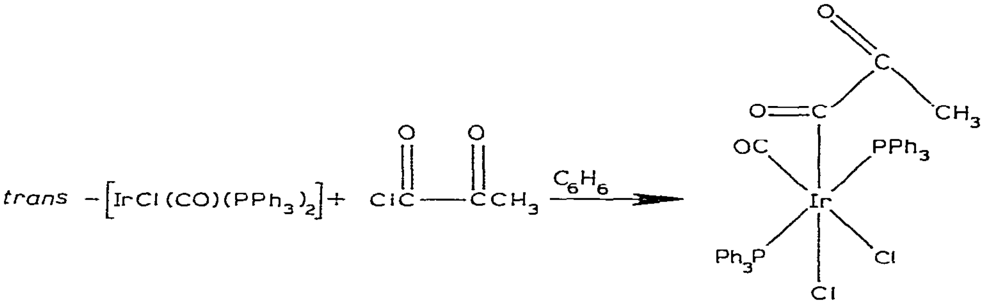
KINETIC DATA FOR MIGRATION REACTIONS OF $\{IrCl_2[C(O)R](PPh_3)_2\}$ IN 1,2-DICHLOROETHANE SOLUTION

	T (°C)	k [a] (sec^{-1}) × 10^4	
R = CH_2Cl	25.9	0.608	$\Delta H^\ddagger$ 22.3 kcal mol^{-1}
	35.1	1.99	$\Delta S^\ddagger$ —3.0 cal K^{-1} mol^{-1}
	44.0	5.56	
	49.5	10.4	
R = $\overset{O}{\overset{\|}{C}}OC_2H_5$	20.9	0.502	$\Delta H^\ddagger$ 22.2 kcal mol^{-1}
	25.1	1.03	$\Delta S^\ddagger$ —2.6 cal K^{-1} mol^{-1}
	34.5	3.11	
	44.3	9.36	
R = CH_2O-C_6H_5	21.0	0.545	$\Delta H^\ddagger$ 20.0 kcal mol^{-1}
	25.0	0.914	$\Delta S^\ddagger$ —9.8 cal K^{-1} mol^{-1}
	34.0	2.53	
	44.1	7.25	

[a] Standard deviations in k are 1—3%.

pyruvoyl complex at 120°C for ca. 4—5 min yields the methyl complex exclusively. This does not occur via an initial acetyl migration followed by CO elimination from the coordinatively saturated acetyl complex since authentic samples of that compound are stable at 120°C indefinitely. DSC scans of the pyruvoyl complex show an asymmetric, exothermic peak with a maximum at 398 K corresponding to a ΔH of —8.9 ± 0.3 kcal mol^{-1}. The weight loss is 4.6 ± 0.3% (calcd. for loss of one CO is 3.3%). The reaction of the pyruvoyl complex in 1,3-dichloroethane solution at 25°C does not follow simple first order kinetics. Solutions are also light-sensitive and decolorize more rapidly in the light than in the dark. Infrared analysis showed that in methylene chloride solution both $[IrCl_2CH_3(CO)(PPh_3)_2]$ and $\{IrCl_2[C(O)CH_3](CO)(PPh_3)_2\}$ are produced either in the light or in the dark. Qualitatively, the ratio of methyl to acetyl product was greater in the dark reaction.

A coordinatively saturated pyruvoyl complex was prepared by addition of pyruvoyl chloride to Vaska's complex (eq. 5). The yellow complex has absorp-



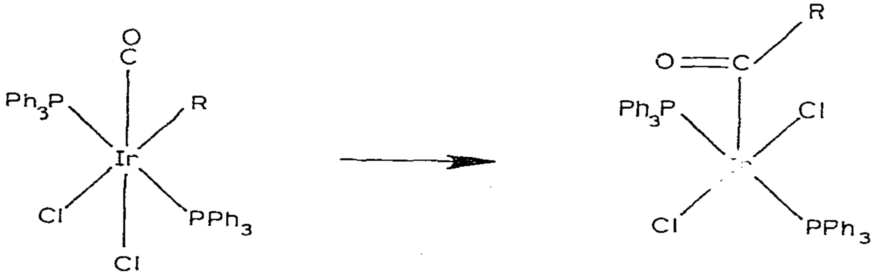
(5)

tion maxima of low intensity at 385 and 440 nm and bands at 1650 and 1706 cm^{-1} assigned to ν(C=O) of the α and β carbonyl groups. These are comparable to those found in $CH_3C(O)C(O)Mn(CO)_5$ [11]. A band at 2036 cm^{-1} is assigned to $\nu(C\equiv O)$ (Table 1). Absorptions in the $\nu(Ir—Cl)$ region were very weak and could not be assigned. The stability of the complex toward loss of CO in solution indicates that CO is not *trans* to the acyl group [5] and the relative intensity of the band at 540 cm^{-1} indicates a *trans*-$Ph_3PIrPPh_3$ structure [12], hence the geometry must be as shown. In contrast to the behavior of the coordinatively unsaturated pyruvoyl complex, the saturated compound is stable toward light as a solid and in solution and thermally stable up to the decomposition point.

Discussion

Combination of our kinetic data with that previously obtained on similar complexes yields the following rates of migration of R, relative to CH_2OPh: $CH_2C_6H_5$ (4.8) > C(O)OEt (1.1) > CH_2OPh (1.00) > CH_2Cl (0.7) > CH_2F (0.2) > CF_3 (0.02) > CHF_2 (0.002) [4,5]. For alkyl groups the general trend is decreasing rate with increasing electronegativity of the substituents. The sp^2 hybridized carbon, C(O)OEt, migrates faster than would be expected based on the electronegativity of its substituents. The activation enthalpies, $\Delta H^{\neq}$, for the migration reaction are in general +20 to +22 kcal mol^{-1} for the groups listed above, with CHF_2 (+25.0) being higher and CH_2Ph (+17.5) being lower. $\Delta S^{\neq}$ values range from —2.6, C(O)OEt, to —15.2, for CH_2Ph.

The ground state ΔH (kcal mol^{-1}) for the migration becomes more exothermic in the order p-$CH_2C_6H_5X$ (—3.3) < CH_3 (—6.5) < CH_2OPh (—7.5) < CH_2Cl (—10.5) < CH_2F (—11.0) < C(O)OEt (—13.7) < CHF_2 (—15.8) < CF_3 (—20.1). Here the trend roughtly parallels the electronegativity of the migrating group. Combination of these ΔH values with $\Delta H^{\neq}$ for the migration allows prediction of $\Delta H^{\neq}$ for the reverse process, CO insertion (eq. 6) [5].The activation enthalpy for insertion to give the coordinatively unsaturated intermediate will range from about +20 kcal for benzyl to +42 kcal for trifluoromethyl with the more electronegative migrating groups having the higher $\Delta H^{\neq}$ values and hence a high kinetic barrier for such processes.



(6)

The origins of the exceptional behavior of the coordinatively unsaturated pyruvoyl complex are not clear at present and further study is required. The known coordinatively saturated pyruvoyl complexes $\{Mn[C(O)C(O)CH_3](CO)_5\}$ [11] and $\{IrCl_2[C(O)C(O)CH_3](CO)(PPh_3)_2\}$ did not show the sensitivity to light or unusual reactivity patterns observed for the coordinatively unsaturated compound.

Experimental

The compound *trans*-[$IrCl(N_2)(PPh_3)_2$] [13], [$IrCl_2(CH_3)(CO)(PPh_3)_2$] [4], {$IrCl_2[C(O)CH_3](CO)(PPh_3)_2$} [4], and $ClC(O)C(O)CH_3$ [14] were prepared by methods in the literature. Other acyl chlorides were prepared by methods in the literature [15] or purchased from Aldrich Chemical Co. Purity was checked by ^1H NMR. Infrared spectra were recorded on a Perkin—Elmer Model 621 spectrometer. ^1H NMR spectra were recorded on a Varian T-60 instrument. Kinetics and electronic spectra were obtained on Cary 14 or 219 spectrometers. Differential scanning calorimetry (DSC) was performed using a Perkin—Elmer Model DSC-2B as previously described [5]. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

{$IrCl_2[C(O)R](PPh_3)_2$} (R = CH_2Cl, CH_2OPh, $CH_2CH_2C(O)OCH_3$, $CH_2C(O)OC_2H_5$, $C(O)OC_2H_5$ or $C(O)CH_3$)

To a suspension of *trans*-[$IrCl(N_2)(PPh_3)_2$] (0.4—0.5 g) in 5 ml benzene or toluene was added 10—20 drops of the acyl chloride, with stirring, in a dry box. The dinitrogen complex gradually dissolved, accompanied by vigorous gas evolution to form a red-orange solution. This required one to two minutes. If precipitation did not occur spontaneously within 2—3 min, ether was added dropwise until solid began to form; then the mixture was cooled in an ice bath. The product was recovered by filtration and washed with ether then dried in vacuo. In the case of ethyl malonyl chloride, an orange solution formed but a light yellow solid precipitated from the solution. The complexes cannot be recrystallized because of the spontaneous migration to give the six-coordinated alkyl—carbonyl complex which occurs in solution. The solids and solutions of the complexes are stable toward air and moisture. Typical yields and physical data are as follows.

CH_2Cl: Orange, m.p. 133—140°C *. Anal. Found: C, 53.15; H, 3.61. Calcd.: C, 52.75; H, 3.73%. Yield, 80%.

CH_2OPh: Orange, m.p. 125—128°C *. Anal. (as toluene solvate) Found: C, 59.87; H, 4.21. Calcd.: C, 60.35; H, 4.47%. Yield, 80%.

$C(O)OC_2H_5$: Red-orange, m.p. 116°C *. Anal. Found: C, 54.15; H, 4.23. Calcd.: C, 54.06; H, 3.97%. Yield, 92%.

$CH_2CH_2C(O)OCH_3$: Orange, m.p. 115—120°C *. Anal. Found: C, 54.74; H, 4.25. Calcd.: C, 54.54; H, 4.13%. Yield, 60%.

$C(O)C(O)CH_3$: Red-orange, m.p. 116°C *. Anal. Found: C, 54.90; H, 4.23. Calcd.: C, 54.55; H, 3.87%. Yield, 60%.

$CH_2C(O)OC_2H_5$: Light yellow, m.p. 223°C, dec. Anal. Found: C, 54.68; H, 4.10. Calcd.: C, 54.60; H, 4.02%. Yield, 76%.

[$IrCl_2(R)(CO)(PPh_3)_2$] (R = CH_2Cl, CH_2OPh, $CH_2CH_2C(O)OCH_3$, $CH_2C(O)OC_2H_5$ or $C(O)OC_2H_5$)

Solid samples of the corresponding coordinatively unsaturated complex, ca. 0.15 g, were either heated in vacuo or under dinitrogen to the transition temperature given above to give quantitative conversion to the product of the alkyl

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* Temperature at which the orange solid turns colorless.

migration reaction. Alternatively, solutions in benzene were refluxed overnight, followed by evaporation to dryness and recrystallization of the solid product from methylene chloride/ether. Physical data are given in Table 1. The complexes are moderately soluble in chlorinated solvents but, in general, not soluble enough to obtain NMR spectra. Physical and analytical data are as follows:

CH_2Cl: Light yellow, m.p. 245°C, dec. Anal. Found: C, 52.57; H, 3.84. Calcd.: C, 52.75; H, 3.73%.

$CH_2OC_6H_5$: Colorless, m.p. 184°C, dec. Anal. Found: C, 56.94; H, 4.07. Calcd.: C, 57.27; H, 4.04%.

$C(O)OC_2H_5$: Light yellow, m.p. 223°C, dec. Anal. Found: C, 53.26; H, 3.95. Calcd.: C, 54.06; H, 3.97%.

$CH_2C(O)OC_2H_5$: Tan, m.p. 225—226°C, dec. Anal. Found: C, 54.82; H, 4.06. Calcd.: C, 54.60; H, 4.02%.

$CH_2CH_2C(O)OCH_3$: Tan, m.p. 233—235°C. dec. Anal. Found: C, 53.53; H, 4.11. Calcd.: C, 54.54; H, 4.13%.

$\{IrCl_2[C(O)C(O)CH_3](CO)(PPh_3)_2\}$

To a suspension of *trans*-$[IrCl(CO)(PPh_3)_2]$, (0.25 g), in 5 ml benzene was added 1 ml pyruvoyl chloride. The color of the mixture gradually became lighter in color over the period of 1 h. The mixture was filtered to give a microcrystalline yellow solid which was washed with ether and dried in vacuo. M.p., 265—268°C, dec. Anal. Found: C, 54.71; H, 4.03. Calcd.: C, 54.18; H, 3:75%. Yield, 90%.

Reactivity of $\{IrCl_2[C(O)C(O)CH_3](PPh_3)_2\}$

A. Solid complex (50 mg) was heated under N_2 at 115°C for five minutes. The orange color gradually faded to a light cream color. The infrared spectrum of the product (Nujol mull or CH_2Cl_2 solution) was identical to that of an authentic sample of $[IrCl_2(CH_3)(CO)(PPh_3)_2]$. A sample of $\{IrCl_2[C(O)CH_3](CO)(PPh_3)_2\}$ treated in the same way was unchanged.

B. Exposure of a solid sample of the five-coordinated pyruvoyl complex, (50 mg) to sunlight and room light in a glass vial, with frequent shaking to expose new surface, for 24 h resulted in the gradual fading of the orange color to a light cream color. Infrared spectra (Nujol mull or CH_2Cl_2 solution) showed the product to be predominantly $\{IrCl_2[C(O)CH_3](CO)(PPh_3)_2\}$ with some $[IrCl_2(CH_3)(CO)(PPh_3)_2]$ present. Qualitatively, the ratio is about 80/20. A parallel sample in a foil-wrapped vial was unchanged by the same treatment.

C. A solution of 20 mg of $\{IrCl_2[C(O)C(O)CH_3](PPh_3)_2\}$ in 0.5 ml CH_2Cl_2, in a glass vial was exposed to room light for 1 h. Infrared spectra of the resulting pale yellow solution showed approximately equal amounts of acetyl and methyl complexes to be present. A sample treated similarly otherwise but kept in the dark appeared to have a higher proportion of methyl complex present.

Kinetics

Decay of the long wavelength maximum of the five-coordinated acyl complexes was monitored using a Cary 219 with thermostated cell holder (temperature constant to ±0.1°C). For each compound at each temperature four different concentration of complex were used and the average rate constant determined. All plots of $\ln(A - A_\infty)$ were linear for at least four half lives.

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