Acidic and Basic Properties of the Hydroxycarbonyl Complex $[IrCl_2(CO_2H)(CO)(PMe_2Ph)_2]$

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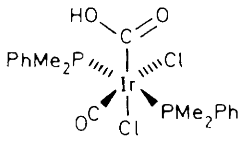
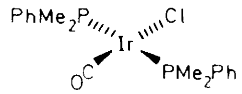
The hydroxycarbonyl compound $[IrCl_2(CO_2H)(CO)(PMe_2Ph)_2]$ (**1**), formed by the rapid reaction of water with the dicarbonyl cation $[IrCl_2(CO)_2(PMe_2Ph)_2]^+$, behaves both as an acid and as a base. The base-catalysed decarboxylation to give $[Ir(H)Cl_2(CO)(PMe_2Ph)_2]$ occurs *via* the compound $[IrCl(CO)(PMe_2Ph)_2]$, but low-temperature ^{31}P and ^1H n.m.r. experiments have failed to identify any intermediate such as $[IrCl_2(CO_2)(CO)(PMe_2Ph)_2]^-$ or $[IrCl(CO_2)(CO)(PMe_2Ph)_2]$. The decarboxylation of such species very rapidly follows deprotonation of the hydroxycarbonyl even at −90 °C. Treatment of (**1**) with $HBF_4 \cdot Et_2O$ leads to dehydroxylation with no observable intermediates whereas CF_3CO_2H reacts initially to give a new species which only gives $[IrCl_2(CO)_2(PMe_2Ph)_2]^+$ with an excess of acid present. This cation exists in solution in two forms. Acetic acid, in contrast, leads to decarboxylation.

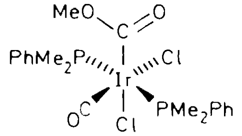
Although the attack of water or hydroxide at carbon monoxide co-ordinated at a transition metal is an important reaction, having been implicated in the reduction of metal ions by CO, in hydride ligand formation, in the water-gas shift reaction, and in other reactions (see, for example, ref. 1), there have been only a few isolated examples of hydroxycarbonyl complexes of type $M-CO_2H$. There have been few detailed studies of their chemistry and no single-crystal structure determinations of CO_2H complexes. The best studied example is the compound $[Fe(CO_2H)(CO)(PPh_3)(\eta\text{-}C_5H_5)]$ [2] and the Ru analogue is also known.[3] Other isolated compounds are $[Mo(CO_2H)(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]$,[4] $[Re(CO_2H)(CO)(N_2R)(C_5H_5)]$ (R = *e.g.* C_6H_4Me-4),[4] $[Re(CO_2H)(CO)(NO)(\eta\text{-}C_5H_5)]$,[5] $[PtCl(CO_2H)(PEt_3)_2]$,[6] and $[Pt(CO_2H)R'\{P(C_6H_{11})_3\}_2]$ (R′ = alkyl, C_6H_{11} = cyclohexyl),[7] while the first reported crystalline sample was $[IrCl_2(CO_2H)(CO)(PMe_2Ph)_2]$.[8] These compounds behave as acids and bases. $[Fe(CO_2H)(CO)(PPh_3)(\eta\text{-}C_5H_5)]$, for example, reacts with acid to give $[Fe(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]^+$ and with base (KOH) to give $K[Fe(CO_2)(CO)(PPh_3)(\eta\text{-}C_5H_5)]$.[2] We have now re-examined the iridium complex above, since it is sufficiently stable for an examination of its acid and base chemistry and, since there is a readily accessible iridium(I) state, the chemistry was expected to be different from that of the iron system.



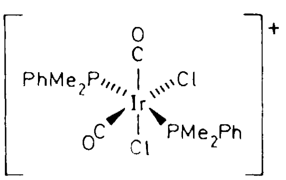
(**1**)



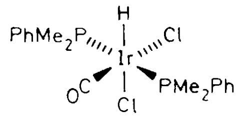
(**2**)



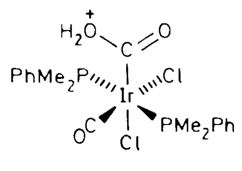
(**3**)



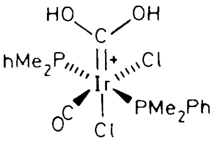
(**4**)



(**5**)



(**6a**)



(**6b**)

Results and Discussion

Synthesis and Characterisation of $[IrCl_2(CO_2H)(CO)(PMe_2Ph)_2]$ (**1**).—Oxidative addition of methyl chloroformate ($ClCO_2Me$) to $[IrCl(CO)(PMe_2Ph)_2]$ (**2**) was previously shown to give the ester $[IrCl_2(CO_2Me)(CO)(PMe_2Ph)_2]$ (**3**).[8] Hydrolysis of the ester was achieved by treatment of a chloroform solution of (**3**) with dry HCl to give a solution containing $[IrCl_2(CO)_2(PMe_2Ph)_2]^+$ (**4**). Removal of the solvent and treatment of (**4**) with H_2O-saturated ether gave compound (**1**).[8] Re-examining this synthesis we have found that a single treatment of this sort gives (**1**) contaminated with (**3**) but that two, or better three, successive treatments with HCl followed by water gives pure compound (**1**). In a single treatment the methanol released by HCl reacts with compound (**4**) on removal of the solvent to regenerate partially the initial compound (**3**). Compound (**1**) was characterised previously by i.r. and low-field room-temperature ^1H n.m.r. spectra; no ^1H n.m.r. signal was assigned to the CO_2H group which was thought to be obscured by the Ph signals.[8] We now find that at −80 °C this group gives a fairly sharp ^1H n.m.r. signal (CD_2Cl_2) at δ 9.40 (s, $\Delta\nu_{\frac{1}{2}}$ = 3 Hz) which broadens at higher temperatures ($\Delta\nu_{\frac{1}{2}}$ = 17 Hz at 20 °C). A separate signal for free water is also observed but this is also broad at 20 °C. Exchange with free water occurs but not rapidly enough to give coalescence at room temperature.

Our attempts to grow good crystals from a $CHCl_3$–light petroleum (b.p. = 40–60 °C) mixture for a single-crystal structure determination led to material contaminated with $[Ir(H)Cl_2(CO)(PMe_2Ph)_2]$ (**5**). Slow crystallisation led to extensive decomposition and a rather poor crystal of (**1**) was selected; even then *X*-ray diffraction data were limited by crystal deterioration in the beam and the final structure was only refined to $R = 0.15$. While the overall co-ordination geometry was confirmed, the structural details, especially those for the CO_2H ligand, are very unreliable and are not reported.[9]

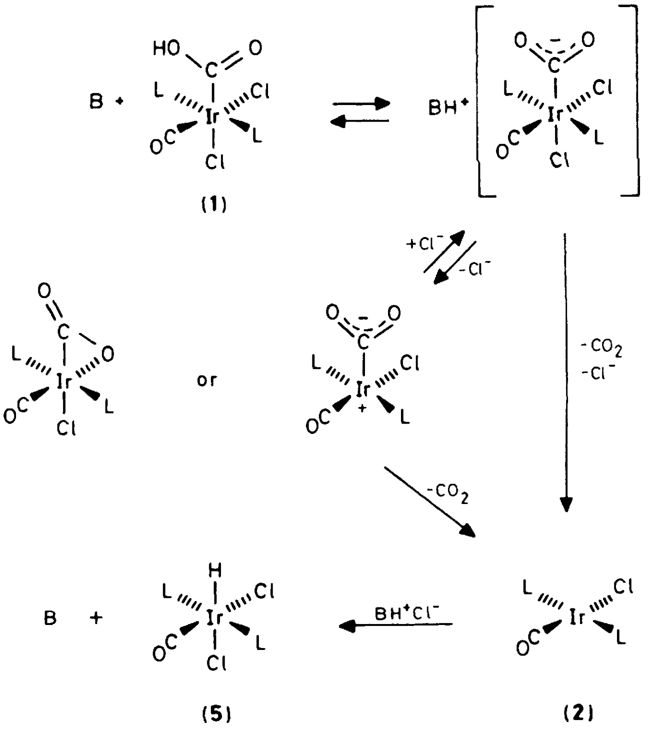
Some samples of compound (**1**) in chloroform solution are unchanged after several hours in air at room temperature but others decompose rapidly. We believe that this is a consequence of both acid- and base-induced reactions described below, many impurities inducing the decompositions. Base rather than acid is most detrimental and acid-free samples seem most sensitive to decomposition.

Reactions of Compound (**1**) *with Base.*—The most characteristic reaction of compound (**1**) is a base-catalysed decarboxylation to give $[Ir(H)Cl_2(CO)(PMe_2Ph)_2]$ (**5**). Addition of tribenzylamine (0.5 mol per mol Ir) to a dichloromethane solution of (**1**) at room temperature leads to the immediate onset of reaction. Infrared absorptions (CH_2Cl_2) at 2 074 and 1 670 cm^{-1} for (**1**) lose intensity to be replaced by those for CO_2 (2 336 cm^{-1}) and the hydride (**5**) [ν(CO) 2 039, ν(IrH) 2 188 cm^{-1}]. After 3 h, no starting material remained. In the early stages a very weak absorption at 1 964 cm^{-1} appeared, remained weak throughout the reaction and finally disappeared as the absorptions due to (**1**) also disappeared. This absorption corresponds to $[IrCl(CO)(PMe_2Ph)_2]$ (**2**), which as an intermediate reaches low steady-state concentration.

Addition of an excess of NEt_3 to a CH_2Cl_2 solution of (**1**) at −90 °C leads immediately and quantitatively to (**2**) (^{31}P n.m.r. evidence) but this is not evidence for either (**5**) or (**2**) being formed first since the hydride (**5**) dehydrochlorinates under these conditions. More informative were ^1H and ^{31}P n.m.r. studies on the addition of tribenzylamine (1 mol per mol Ir) to compound (**1**) in dichloromethane at low temperatures. After 1 h at −50 °C the ^{31}P n.m.r. spectrum showed a signal for compound (**2**) which had grown strongly (30% of total signal) while that for the hydride (**5**) was still very weak (5% of total). After 2.5 h the signal for (**5**) had increased markedly but still compound (**2**) predominated. On warming to room temperature essentially all the iridium was present as the hydride (**5**). On cooling again to −50 °C, the spectrum remained unchanged; the iridium(I) species did not reform. We have shown separately that tribenzylamine hydrochloride reacts readily with an equimolar amount of (**2**) to give the hydride (**5**) at room temperature.

Thus compound (**2**) is the initial kinetically favoured product of decarboxylation and furthermore no ^{31}P signal was observed, even on treating (**1**) with base at −90 °C, that might have been ascribable to the conjugate anion $[IrCl_2(CO_2)(CO)(PMe_2Ph)_2]^-$ or a neutral CO_2 complex formed by loss of Cl^-. Decarboxylation occurs rapidly even at −90 °C to give the iridium(I) complex which is protonated slowly at −50 °C but rapidly at room temperature. Either there is an initial rapid pre-equilibrium between (**1**) and its conjugate anion, which is present only in very low concentrations and which decarboxylates fairly slowly, or it is the initial deprotonation that is rate-determining with decarboxylation occurring rapidly. The former, which seems more likely, implies that compound (**1**) is a much weaker acid than organic carboxylic acids. We cannot distinguish synchronous from successive decarboxylation and chloride loss but since $[IrCl(CO)(PMe_2Ph)_2]$ does not react with CO_2 the decarboxylation is irreversible. Scheme 1 is proposed.

These general results contrast with the deprotonation of $[Fe(CO_2H)(CO)(PPh_3)(\eta\text{-}C_5H_5)]$ which gives an isolable conjugate anion which is very much more stable to decarboxylation than the parent CO_2H complex.[2] Similarly $[Mo(CO_2H)(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]$ does not decarboxylate on treatment with NEt_3.[3] In contrast, $[Re(CO_2H)(CO)(NO)(\eta\text{-}C_5H_5)]$ readily gives the hydride with strong base as catalyst.[5] It would seem that, if there is a stable oxidation state of the metal two below that of the CO_2H complex, deprotonation leads rapidly to decarboxylation otherwise the conjugate anion is stable. However, factors favouring a relatively stable lower oxidation state are also those favouring higher acidity and it is not obvious how to separate the effects of acidity and basicity from redox effects in decarboxylation.



Scheme 1. L = PMe_2Ph, B = base

Reaction of Compound (**1**) *with Acid.*—The reaction of (**1**) with $HBF_4\cdot Et_2O$ is straightforward. As increasing amounts of acid are added to a CH_2Cl_2 solution of (**1**) the strong carbonyl absorptions at 2 074 and 1 670 cm^{-1} are gradually replaced by new absorptions at 2 154 and 2 116 cm^{-1} consistent with the cationic dicarbonyl (**4**), which is formed completely after the addition of 1 mol equiv. of acid. Rather different behaviour is observed using trifluoroacetic acid. With a large excess of acid present the spectrum (2 142 and 2 101 cm^{-1}) is similar (except for the lower frequencies) to that of (**4**) formed using $HBF_4\cdot Et_2O$. The lower frequencies for $[IrCl_2(CO)_2(PMe_2Ph)_2][CF_3CO_2]$ compared with the BF_4^- salt probably indicate greater cation–anion interaction with $CF_3CO_2^-$. Recording the i.r. spectrum of a CH_2Cl_2 solution of (**1**) on successive additions of CF_3CO_2H indicates that there are intermediates (Figure). On adding only 2 mol of CF_3CO_2H per mol of Ir, the absorption at 1 670 cm^{-1} is *ca.* 20% of its original intensity while the metal carbonyl absorption loses no intensity but shifts from 2 074 to 2 078 cm^{-1}. After 5 mol equiv. of CF_3CO_2H had been added the peak at 2 078 cm^{-1} had started to weaken while that at 1 670 cm^{-1} was absent.

The species (**6**) giving the absorption at 2 078 cm^{-1} is either a hydrogen-bonded adduct between (**1**) and CF_3CO_2H or it is protonated compound (**1**) (formed without loss of OH^-). We believe that it is the latter because of the large change in the spectrum around 1 670 cm^{-1} and because extremely similar spectra are also obtained on addition of CF_3CO_2H to (**3**). Intermediate (**6**) may be one of the protonated forms (**6a**) or (**6b**).

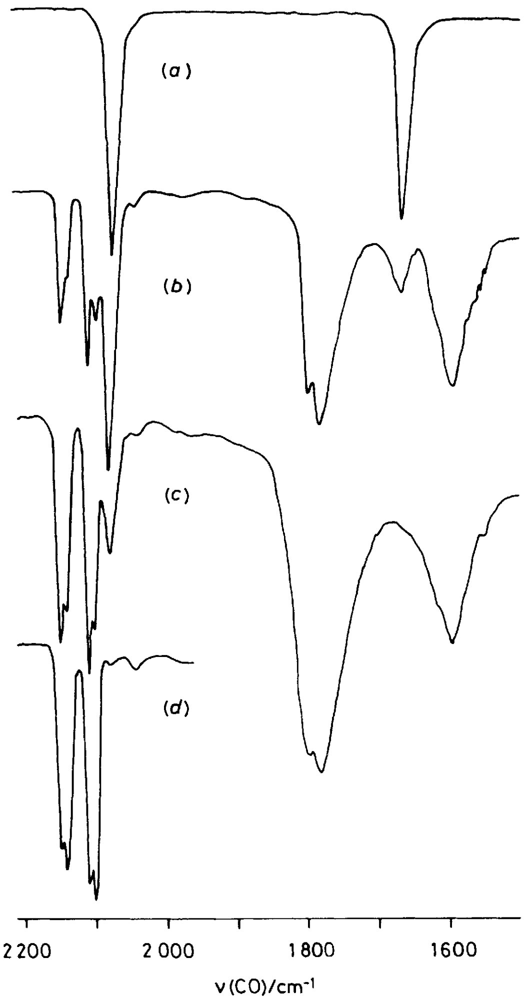
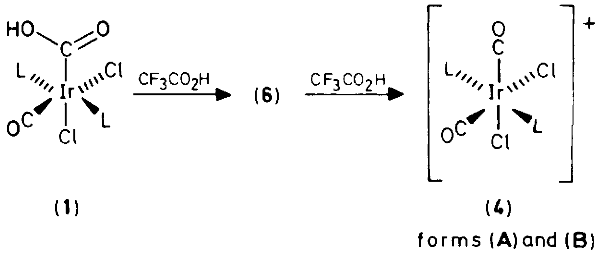


Figure. Spectra [ν(CO)] of solutions of $[IrCl_2(CO_2H)(CO)(PMe_2Ph)_2]$ (**1**) in dichloromethane on addition of increasing amounts of CF_3CO_2H: (*a*) 0, (*b*) 2.0, (*c*) 5.0, and (*d*) 13.0 mol of acid per mol (**1**)

Presumably (**6a**) would be the species formed initially on treatment of cation (**4**) with water and an intermediate in the formation of (**1**) from (**4**). Since in CH_2Cl_2 the cation (**6**) is very likely to be involved in an intimate hydrogen-bonded ion pair with trifluoroacetate, a H-bonded adduct of (**1**) with CF_3CO_2H and the proposed forms (**6a**) and (**6b**) may be indistinguishable. Increasing the concentration of CF_3CO_2H leads to (**4**) which appears in two forms, (**A**) and (**B**), each of which give two ν(CO) absorptions: at 2 148 and 2 109 cm^{-1} (predominating at lower acid concentrations) and at 2 142 and 2 101 cm^{-1} (predominating at higher acid concentrations). These are likely to be due to the same complex cation (**4**) involved in different solution forms differing in their mode of ion pairing/hydrogen bonding. Following the reaction of compound (**1**) with CF_3CO_2H by ^1H n.m.r. showed only the replacement of methyl signals of compound (**1**) by those for compound (**4**). Presumably the species present prior to C–O cleavage are in rapid exchange as are the different solution forms of cation (**4**).

Acetic acid behaves quite differently. The addition of 10 mol of acid per mol of (**1**) leads to decarboxylation to give $[Ir(H)Cl_2(CO)(PMe_2Ph)_2]$ (**5**). We believe that this acid is too weak to shift the equilibrium very much towards (**4**) but that the acetate ion formed along with (**4**) induces a base-catalysed decarboxylation. The reactions (1)—(3) are proposed to explain this effect (L = PMe_2Ph).



Scheme 2. L = PMe_2Ph

$$[IrCl_2(CO_2H)(CO)L_2] + CH_3CO_2H \rightleftharpoons [IrCl_2(CO)_2L_2]^+ + CH_3CO_2^- \quad (1)$$

$$[IrCl_2(CO_2H)(CO)L_2] + CH_3CO_2^- \rightleftharpoons [IrCl_2(CO_2)(CO)L_2]^- + CH_3CO_2H \quad (2)$$

$$[IrCl_2(CO_2)(CO)L_2]^- + CH_3CO_2H \longrightarrow [IrHCl_2(CO)L_2] + CH_3CO_2^- + CO_2 \quad (3)$$

Experimental

Nuclear Magnetic Resonance Spectra.—Hydrogen-1 n.m.r. spectra were recorded in $CDCl_3$ or CD_2Cl_2 solution on a Varian XL200 spectrometer. Phosphorus-31 n.m.r. spectra were recorded in dichloromethane solution on the same instrument operating at 81 MHz using $P(OMe)_3$ in $[^2H_8]$toluene as an external reference/lock.

Infrared Spectra.—These were recorded on a Perkin-Elmer 983 spectrometer. Samples were recorded either as Nujol mulls between NaCl plates or in dichloromethane solution in CaF_2 solution cells.

Compounds (**2**),[10] (**5**),[10] and (**3**)[8] were prepared by literature methods. Compound (**1**) was also prepared as reported[8] except that the method was slightly modified and improved as described below.

Preparation of $[IrCl_2(CO_2H)(CO)(PMe_2Ph)_2]$ (**1**).—Hydrogen chloride gas was passed through a solution of $[IrCl_2(CO_2Me)(CO)(PMe_2Ph)_2]$ (0.223 g) in ethanol-free chloroform (3 cm^3) for 1 min. The solvent was removed under vacuum to give a slightly green oil. Addition of water-saturated ether (5 cm^3) gave a white crystalline solid which was shown to be a mixture of compounds (**1**) and (**3**). Redissolving in ethanol-free chloroform and a second treatment with HCl, then water-saturated ether, gave the product (**1**) as white crystals (0.135 g). I.r.: ν(OH) 3 295ms, ν(CO) 2 073 and 1 670 cm^{-1} (Nujol); ν(CO) 2 074 and 1 670 cm^{-1} (CH_2Cl_2). ^1H N.m.r. (CD_2Cl_2): δ 2.07 (t, $^2J_{PH} + ^4J_{PH} = 8.4$), 2.15 (t, $^2J_{PH} + ^4J_{PH} = 9.0$ Hz), 9.40 (br, $\Delta\nu_{\frac{1}{2}}$ = 3 Hz at − 80 °C, 17 Hz at 20 °C). ^{31}P N.m.r. (CH_2Cl_2): δ −168.1.

Treatment of $[IrCl_2(CO_2H)(CO)(PMe_2Ph)_2]$ (**1**) *with Acid.*—*With* $HBF_4{\cdot}Et_2O$. Successive amounts of $HBF_4{\cdot}Et_2O$ (0.2, 0.4, 0.6, 0.8, and 1.0 mol per mol of Ir) were injected into a solution of compound (**1**) (0.010 g) in dichloromethane (2.0 cm^3) at room temperature and the i.r. spectra recorded. The formation of $[IrCl_2(CO)_2(PMe_2Ph)_2][BF_4]$ was monitored by the growth of absorptions at 2 154 and 2 116 cm^{-1} and was found to be complete after the addition of 1.0 mol equiv. of acid.

With CF_3CO_2H. A similar treatment with CF_3CO_2H gave the rather more intricate spectra shown in the Figure. Monitoring the ^1H n.m.r. spectrum on adding CF_3CO_2H in increasing amounts to a solution of (**1**) (0.022 g) in CD_2Cl_2 (0.6

cm^3) at 20 °C showed the replacement of the signals for (**1**) by those for the cation (**4**) [δ 2.26 (t, $^2J_{PH} + {}^4J_{PH} = 9.1$ Hz)] with no other signals being observed. See Scheme 2.

Treatment of [$IrCl_2(CO_2H)(CO)(PMe_2Ph)_2$] (**1**) *with Base.*—*With tribenzylamine.* A solution of (**1**) (0.030 g) in CH_2Cl_2 (2.5 cm^3) in an n.m.r. tube was cooled to −55 °C and $N(CH_2Ph)_3$ (0.014 g) added and changes in the ^{31}P n.m.r. spectra were followed with time. The signal for (**1**) was successively replaced by that for [$IrCl(CO)(PMe_2Ph)_2$] (δ −146.4) which was itself replaced by that for [$Ir(H)Cl_2(CO)(PMe_2Ph)_2$] (δ −166.0). After 4 h this was the only absorption present apart from a few weak absorptions around δ −162 which we have not identified.

With triethylamine. NEt_3 (0.01 cm^3) was added to a solution of (**1**) (0.022 g) in CH_2Cl_2 (2.5 cm^3) at −90 °C which immediately changed from very pale to bright yellow. The first ^{31}P n.m.r. spectrum obtained after 1 min at −90 °C showed only the presence of [$IrCl(CO)(PMe_2Ph)_2$]. No further change occurred with time.

Acknowledgements

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