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MODIFICATION OF THE ACID-BASE PROPERTIES OF HYDROXYCARBONYL COMPLEXES OF IRIDIUM(III) BY SUBSTITUTION OF CARBON MONOXIDE BY A TERTIARY PHOSPHINE LIGAND

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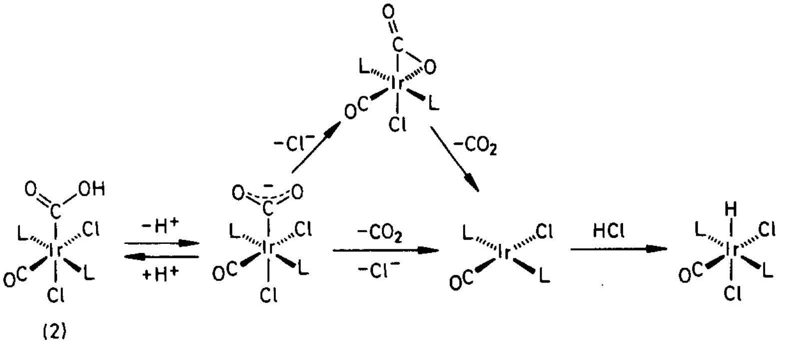
Summary

A dichloromethane solution of the cationic carbonyl complex $[IrCl_2(CO)(PMe_2Ph)_3][ClO_4]$ reacts with aqueous KOH to give $[IrCl_2(CO_2H)(PMe_2Ph)_3]$ which has been characterised spectroscopically. This CO_2H compound is very much more basic and very much less acidic than $[IrCl_2(CO_2H)(CO)(PMe_2Ph)_2]$. Tertiary amines will not deprotonate $[IrCl_2(CO_2H)(PMe_2Ph)_3]$ while $Li[N(SiMe_3)_2]$ leads to decarboxylation products *trans*, *mer*- and *cis*, *mer*-$[IrHCl_2(PMe_2Ph)_3]$. The mechanisms of these reactions are considered and the hydroxycarbonyl complex is compared with its formato isomer which decarboxylates much less readily.

Introduction

The first hydroxycarbonyl complex to be isolated was $[IrCl_2(CO_2H)(CO)(PMe_2Ph)_2]$ (**2**), a complex formed by the reaction of $[IrCl_2(CO)_2(PMe_2Ph)_2]^+$ (**1**) with water [1]. The CO_2H complex undergoes base-catalysed (tribenzylamine) de-



Scheme 1 (L = PMe₂Ph)

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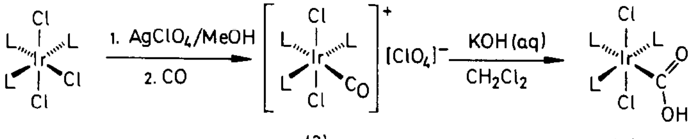
carboxylation by a redox pathway involving reduction to [$IrCl(CO)(PMe_2Ph)_2$] via [$IrCl_2(CO_2)(CO)(PMe_2Ph)_2$]$^-$ and/or [$IrCl(CO_2)(CO)(PMe_2Ph)_2$] (Scheme 1) [2]. The chemistry of compounds of type L_nM-CO_2H is extremely dependant upon the metal M and the other ligands L. Sometimes rapid loss of CO_2 follows deprotonation as in Scheme 1, while in other cases the conjugate anion is indefinitely stable as when [$Fe(CO_2H)(CO)(PPh_3)(C_5H_5)$] is deprotonated with KOH in which case the CO_2H compound decarboxylates more readily than the anion [3]. We now wish to report the synthesis of *trans*, *mer*-[$IrCl_2(CO_2H)(PMe_2Ph)_3$] (**4**), from *trans, mer*-[$IrCl_2(CO)(PMe_2Ph)_3$][ClO_4] (**3**) by reaction with KOH and a comparison of the chemistries of compounds **2** and **4** and a comparison of **4** with the isomeric formato complex **5**.

Results and discussion

Synthesis of trans, mer-[$IrCl_2(CO_2H)(PMe_2Ph)_3$]

The compound *mer*-[$IrCl_3(PMe_2Ph)_3$] reacts with $AgClO_4$ in acetone containing a little water to give [$IrCl_2(H_2O)(PMe_2Ph)_3$][ClO_4] [4,5]. When the reaction is carried out in methanol, again containing traces of water, a solution containing [$IrCl_2(H_2O)(PMe_2Ph)_3$][ClO_4] and [$IrCl_2(MeOH)(PMe_2Ph)_3$][ClO_4] is obtained. Bubbling CO into this solution gives *trans*, *mer*-[$IrCl_2(CO)(PMe_2Ph)_3$][ClO_4] (**3**), which may be isolated as pale yellow crystals (see Scheme 2). This compoud has previously been synthesised from CO and [$IrCl_2(NO_3)(PMe_2Ph)_3$] in the presence of $NaClO_4$ [6]. Unlike [$IrCl_2(CO)_2(PMe_2Ph)_2$]$^+$ (**1**) which is so electrophilic that it reacts rapidly with traces of water [2], [$IrCl_2(CO)(PMe_2Ph)_3$]$^+$ (**3**) is very much less electrophilic and does not react with water. The donor properties of PMe_2Ph are much higher than those of CO and the introduction of the third phosphine ligand increases back-donation to the remaining carbonyl ligand. The reduced electrophilicity of the CO in **3** is indicated by the quite low value of ν(CO) (2102 cm^{-1}). A reduced tendency toward hydroxycarbonyl ligand formation upon substituting CO by tertiary phosphine has also been observed in other systems. The cations [$Re(CO)_2(NO)(\eta\text{-}C_5H_5)$][$BF_4$] [7] and [$Fe(CO)_2(PPh_3)(\eta\text{-}C_5H_5$][Cl] [3] both react with hydroxide ion to give the corresponding hydroxycarbonyl complexes. However, [$Re(CO)L(NO)(\eta\text{-}C_5H_5)$][$BF_4$] ($L = PPh_3$ or PMe_2Ph) is unreactive towards hydroxide ion [7], whilst [$Fe(CO)(dppe)(\eta\text{-}C_5H_5)$][Cl] (dppe = $Ph_2PCH_2CH_2PPh_2$) reacts to give only [$Fe(CO)(dppe)(\eta\text{-}C_5H_5)$][OH] [3]. Very large variations of electrophilicities are observed on replacing CO by a tertiary phosphine.

However, a dichloromethane solution of **3** does react with an approximately three-fold excess of aqueous potassium hydroxide to give [$IrCl_2(CO_2H)(PMe_2Ph)_3$]



(3) (4)

Scheme 2 ($L = PMe_2Ph$)

TABLE 1

INFRARED AND ^{1}H AND ^{31}P NMR DATA

Complex	$\delta(^1H)$ [a] (ppm)	$\delta(^{31}P)$ [b] (ppm)	ν(CO) [c] (cm^{-1})
$[IrCl_2(CO)(PMe_2Ph)_3][ClO_4]$ (3)	1.73d [J(PH) 10.8] [d] 1.78t [J(PH) 8.3]	−186.0d [J(PP) 26] [c] −190.7t	2102
$[IrCl_2(CO_2H)(PMe_2Ph)_3]$ (4)	1.09d [J(PH) 8.4] [d] 1.69t [J(PH) 8.2] 10.0s [CO_2H]	−182.6d [J(PP) 21] [f] −193.7t	1672
$[IrCl_2(HCO_2)(PMe_2Ph)_3]$ (5)	1.29d [J(PH) 11.1] [e] 1.71t [J(PH) 8.3] 8.88d [HCO_2,^4J(PH) 2]	−176.6d [J(PP) 18] [f] −195.5t	1637

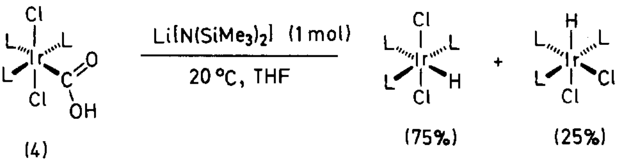
[a] J in Hz. [b] ^{31}P signals referenced to P(OMe)$_3$ in C_6D_6. [c] In CH_2Cl_2. [d] In CD_2Cl_2. [e] In $CDCl_2$. [f] In THF.

(4) in the CH_2Cl_2 layer which may be isolated as yellow crystals. The corresponding ester $[IrCl_2(CO_2Me)(PMe_2Ph)_3]$ was previously formed by treating the same cationic carbonyl complex with sodium methoxide in methanol [6]. The CO_2H and CO_2Me complexes are closely related spectroscopically. A Nujol mull of the CO_2H species **4** shows ν(CO) at 1672 cm^{-1} and two weak absorptions at 3334 and 3303 cm^{-1} due to ν(OH). The configuration is established by ^{1}H and ^{31}P NMR data (Table 1).

No single crystal X-ray structure has been reported for a CO_2H complex and attempts were made to establish that for compound **4**. Difficulty was found in recrystallisation, oils being frequently obtained. Eventually a single crystal was obtained by the slow diffusion of diethyl ether into a dichloromethane solution of compound **4** at −20°C. The X-ray crystal structure of compound **4** was determined and will be presented elsewhere [8]. This confirmed that **4** has the *mer,trans*-configuration and contains the carbon-bonded CO_2H ligand *trans* to a PMe_2Ph ligand. Although the CO_2H ligand was shown to be perpendicular to the plane of the three phosphorus atoms, in solution there is a time-averaged plane of symmetry through the IrP_3 set of atoms since the Me groups of the *trans* pair of PMe_2Ph ligands do not appear to be diastereotopic as expected for a static structure. Either there is a rapid rotation about the Ir–CO_2H bond or a rapid proton transfer between the two oxygen atoms. Likewise for $[IrCl_2(CO_2Me)(PMe_2Ph)_3]$ [6] there is a single triplet in the ^{1}H NMR spectrum for the *trans*-phosphines so that rapid rotation seems that most likely. A broad resonance at δ 10.0 in the NMR spectrum of **4** in CD_2Cl_2 is assigned to the hydroxycarbonyl group. This signal sharpens at low temperatures ($\Delta\nu_{\frac{1}{2}}$ 3 Hz at −70°C) but no coupling to the *trans*-^{31}P nucleus is observed.

Reactions of $[IrCl_2(CO_2H)(PMe_2Ph)_3]$ (4) with acids and bases

The hydroxycarbonyl compound **4** reacts quantitatively with CF_3CO_2H (1 mol/mol Ir) in CH_2Cl_2 to generate $[IrCl_2(CO)(PMe_2Ph)_3][CF_3CO_2]$. This contrasts with the behaviour of $[IrCl_2(CO_2H)(CO)(PMe_2Ph)_2]$ (**2**) which requires an excess of CF_3CO_2H (ca. 10 mol/mol Ir) to effect complete dehydroxylation [2]. Compound **4** may even be dehydroxylated by acetic acid. ^{31}P NMR signals for **4** are successively replaced by those for **3** on adding increasing amounts of CH_3CO_2H, reaction being



Scheme 3 (L = PMe_2Ph)

essentially complete after the addition of 10 mol acid/mol Ir. Thus $[IrCl_2(CO_2H)(PMe_2Ph)_3]$ (**4**) is vastly more basic and presumably vastly less acidic than $[IrCl_2(CO_2H)(CO)(PMe_2Ph)_2]$. A reasonable measure of the difference is the difference between CF_3CO_2H (pK_a 0.3) and CH_3CO_2H (pK_a 4.75).

The compound $[IrCl_2(CO_2H)(CO)(PMe_2Ph)_2]$ is very sensitive towards base, undergoing base-induced decarboxylation as in Scheme 1. In marked contrast $[IrCl_2(CO_2H)(PMe_2Ph)_3]$ (**4**) is formed in the presence of an excess of hydroxide ion. We have confirmed that bases, in general, have no effect on **4** by showing that the CO_2H NMR signal at δ 10.0 is changed in no way by the addition of tribenzylamine or an excess of triethylamine. No measurable conversion of **4** to $[NHR_3]^+$ $[IrCl_2(CO_2)(PMe_2Ph)_3]^-$ occurs under these conditions. When dry THF solutions of **4** are treated with $Li[N(SiMe_3)_2]$ (1 mol per mol Ir) at 20°C, the formation of two decarboxylation products occurs over 2 to 3 h. The *cis*, *mer*- and *trans*, *mer*-isomers of $[IrHCl_2(PMe_2Ph)_3]$ [11] are formed as shown in Scheme 3. ^{31}P NMR studies of this reaction at −60°C show the presence of intermediates. One intermediate formed immediately gives a ^{31}P NMR doublet and triplet [δ − 181.1(d) and −193.4(t), J 21 Hz] close in chemical shift to the signals for $[IrCl_2(CO_2H)(PMe_2Ph)_3]$ (**4**) and we assign these signals to $[IrCl_2(CO_2)(PMe_2Ph)_3]^-$. Another intermediate also gives a set of triplet and doublet patterns [δ − 163.3(t) and −146.8(d); J 26 Hz] expected for a *mer*-complex but around 30 ppm lower than the usual iridium(III) region and we assign these to $[IrCl(PMe_2Ph)_3]$. Also an unassigned ^{31}P NMR singlet (δ − 166) was observed.

The decarboxylation route is complex. It seems that the major hydride product, *trans*, *mer*-$[IrHCl_2(PMe_2Ph)_3]$ (75%) is formed faster than the thermodynamically more stable minor isomer *cis*, *mer*-$[IrHCl_2(PMe_2Ph)_3]$ (25%) which is only formed in the later stages of the reaction as the signals we have assigned to iridium(I) disappear. A reductive decarboxylation route via $[IrCl(PMe_2Ph)_3]$ would be expected to lead to the *cis,mer*-isomer by oxidative addition. Accordingly we believe that the major *trans,mer*-product is formed directly from $[IrCl_2(CO_2)(PMe_2Ph)_3]^-$ and not via reduction to iridium(I). Thermal treatment of **4** in refluxing THF (3 h) also leads mainly to the *trans,mer*-isomer but also to a little of the *cis,mer*-isomer.

We have synthesised the formato complex *trans,mer*-$[IrCl_2(HCO_2)(PMe_2Ph)_3]$ (**5**), isomeric with **4**, by treatment of *mer*-$[IrCl_3(PMe_2Ph)_3]$ with thallium(I) formate in methanol. Complex **5** was obtained slightly contaminated by $[IrCl_3(PMe_2Ph)_3]$ and *trans,mer*-$[IrHCl_2(PMe_2Ph)_3]$ and was characterised by ^1H and ^{31}P NMR and infrared data [ν(CO) 1637 and ν(CH) 2698 cm^{-1}]. The formato group gives a sharp ^1H NMR doublet at δ 8.87 in $CDCl_3$ as a result of coupling (^4J) to the *trans*-phosphorus. Unlike **4**, complex **5** does not decarboxylate in refluxing THF over 3 h. This agrees with the results obtained for $[Fe(CO)_2(HCO_2)(\eta\text{-}C_5H_5)]$ which was found to be much more stable than the hydroxycarbonyl isomer $[Fe(CO)_2(CO_2H)(\eta\text{-}C_5H_5)]$ [12].

Final comment

While the number of tertiary phosphine ligands present seems to control the reactivity of the CO_2H ligand, we have considered the possibility that the difference between $[IrCl_2(CO_2H)(PMe_2Ph)_3]$ (**4**) and $[IrCl_2(CO_2H)(CO)(PMe_2Ph)_2]$ (**2**) may be in part due to the CO_2H ligand being *trans* to PMe_2Ph or Cl respectively. This sort of difference has a marked influence on the acidity of hydride ligands. For example, in the isomer of $[IrHCl_2(CO)(PR_3)_2]$ with *trans*-phosphines and *cis*-chlorides the hydride is much more acidic than in the isomer with *trans*-phosphines and *trans*-chlorides [13].

It was believed that hydride *trans* to chloride is more acidic than one *trans* to a carbonyl or phosphine ligand because of a greater polarisation of σ-electron density towards the chloride ligand. Clearly *trans*-influences can be important. The complex *cis,mer*-$[IrCl_2(CO)(PMe_2Ph)_3]^+$ has a lower value for $\nu(CO)$ [2070 cm^{-1}] than the *trans,mer*-isomer **3** [2105 cm^{-1}] [6]. The CO ligand (*trans* to chloride) in the *cis,mer*-isomer should be less electrophilic and the derived CO_2H complex less acidic. We have found, however, that the reaction of the *cis,mer*-carbonyl cation with hydroxide ion gave an intractable mixture and so we have been unable to pursue these ideas further.

Experimental

mer-$[IrCl_3(PMe_2Ph)_3]$ was prepared as reported [11].

Synthesis of $[IrCl_2(CO)(PMe_2Ph)_3][ClO_4]$

A suspension of *mer*-$[IrCl_3(PMe_2Ph)_3]$ (0.616 g) was shaken with $AgClO_4$ (0.196 g) in methanol (25 cm^3) for 15 min. A white precipitate of silver chloride was filtered off to leave a bright clear yellow filtrate. Carbon monoxide was bubbled through the solution for 30 min to give a pale yellow solution. Removal of the solvent under reduced pressure gave a pale yellow solid which was recrystallised by dissolving in dichloromethane and precipitating with diethyl ether to give the product as pale yellow crystals (0.488 g) characterised by comparison with reported data for this compound and by analysis (Found: C, 37.1; H, 4.15; Cl, 13.2. $C_{25}H_{33}Cl_3IrO_5P$ calcd.: C, 37.3; H, 4.15; Cl, 13.2%). Use of $AgBF_4$ gave $[IrCl_2(CO)(PMe_2Ph)_3][BF_4]$ (95%) as almost colourless crystals (Found: C, 37.6; H, 4.25 Cl, 9.1; P, 11.7. $C_{25}H_{33}BCl_2F_4IrP_3$ calcd.: C, 37.9; H, 4.2; Cl, 8.95; P, 11.75%).

Synthesis of $[IrCl_2(CO_2H)(PMe_2Ph)_3]$

Aqueous potassium hydroxide (0.17 mol dm^{-3}, 10.0 cm^3) was added to a solution of $[IrCl_2(CO)(PMe_2Ph)_3][ClO_4]$ (0.381 g) in dichloromethane (12 cm^3). The two-phase mixture was shaken for several minutes during which the dichloromethane layer became bright yellow. This layer was separated, filtered, and evaporated under reduced pressure to give a yellow oil. Addition of diethyl ether (ca. 10 cm^3) give the product as yellow crystals (0.252 g) (Found: C, 41.8; H, 4.95; Cl, 10.0; P, 12.8. $C_{25}H_{34}Cl_2IrO_2P_3$ calcd.: C, 42.5; H, 4.65; Cl, 9.65; P, 12.65%).

Synthesis of [$IrCl_2(HCO_2)(PMe_2Ph)_3$]

Thallium(I) formate (0.292 g) was added to a solution of *mer*-[$IrCl_3(PMe_2Ph)_3$] (0.333 g) in methanol (30 cm^3) and dichloromethane (5 cm^3) and the mixture shaken for 20 min. A white precipitate of thallium(I) chloride was removed by filtration and the yellow filtrate reduced to dryness under reduced pressure. The residue was dissolved in dichloromethane (10 cm^3), the solution filtered and the solvent removed to give a yellow oil. Addition of diethyl ether (5 cm^3) gave the product as yellow crystals (0.131 g). The ^1H NMR spectrum ($CDCl_3$) showed the presence of *mer*-[$IrCl_3(PMe_2Ph_3$] and *trans,mer*-[$IrHCl_2(PMe_2Ph)_3$] (ca. 5% of total signal) in addition to the formato complex. These impurities probited good elemental analysis. but the product was characterised spectroscopically.

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