Activation of Ring Methyls in Pentamethylcyclopentadienyliridium(III); New Routes to Functionalised Complexes

Jesus A. Miguel-Garcia and Peter M. Maitlis*
Department of Chemistry, The University, Sheffield S3 7HF, UK

Pentamethylcyclopentadienyliridium(III) complexes, *e.g.* [($C_5Me_4CH_3$)Ir(Me)(Ph)(CO)] are metallated by Bu^sLi at a ring methyl; the resultant lithio-complex reacts with organic halides, ketones and CO_2 to give the appropriately substituted [($C_5Me_4CH_2W$)IrX(Me)(CO)] (X = Ph; W = $SiMe_3$, CH_2=$CHCH_2$, $PhCH_2$, Ph_2COH, PhMeCOH, or X = Cl; W = CO_2H, CO_2Me).

The pentamethylcyclopentadienyliridium complexes have attracted substantial attention since their discovery in 1969,[1] since the combination of an inert and stable ring-to-metal bond on one side of the metal and high lability of the ligands on the other side, has allowed many stoicheiometric and catalytic reactions to be carried out without loss of the stabilising ring.[2]

Although complexes containing related rings, C_5Me_4R, are known,[3] they have to be prepared from the appropriately substituted cyclopentadienyls. These are not always easy to access, and the method of preparation severely limits the functional groups which may be introduced. We herein describe simple procedures for the monosubstitution of one ring methyl hydrogen (in **1**) by lithium and its replacement by a wide variety of other groups (W) (Scheme 1). The reaction makes use of an early discovery that the ring hydrogens in a number of [$C_5Me_5ML_n$] compounds (M = Rh, Ir) are quite easily exchanged for deuterium in D_2O/OD^-,[4] suggesting some stability for the [$C_5Me_4CH_2ML_n$]$^-$ anion. A number of related reactions are known, for example, the polysubstitution of [$Co(C_5H_5)(C_5Me_5)$]$^+$ by Bu^tOK/MeI has recently been reported.[5]

Treatment of a solution of **1**[6] in tetrahydrofuran (THF) at −78 °C with one equivalent of s-butyllithium (1.3 mol dm^{-3} in cyclohexane, Aldrich) caused a change from colourless to yellow, probably due to the presence of the lithium complex **2**. On reaction of this yellow solution with trimethylchlorosilane, benzyl chloride, or allyl bromide, the colour disappeared again and, on work-up, the complexes **3a–c** were obtained (89, 70 and 91% yields respectively).†

The lithio-intermediate **2** also reacted with ketones; *e.g.* benzophenone and acetophenone gave **3d**‡ (77%) and **3e** (79%) respectively, after hydrolysis and work-up. These alcohols show strong, sharp ν(OH)/cm^{-1} at 3598 **3d** and 3555 **3e**, suggesting little H-bonding.

In all the complexes **3a–e** four signals were observed in the C_5Me_4 region, both in the ^1H and the ^{13}C NMR spectra, as expected for two pairs of diastereotopic methyls. This is a consequence of the three inequivalent ligands on the other side, and the consequent chiral centre at the metal.

Intermediate **2** also reacted with carbon dioxide; after hydrolysis a product was obtained, with elemental analyses and spectroscopic data consistent with **3f**, [($C_5Me_4CH_2CO_2$-Li)Ir(CO)(Me)(Ph)] [ν(CO_2) 1747 (w, br.) 1714 (w-med.);

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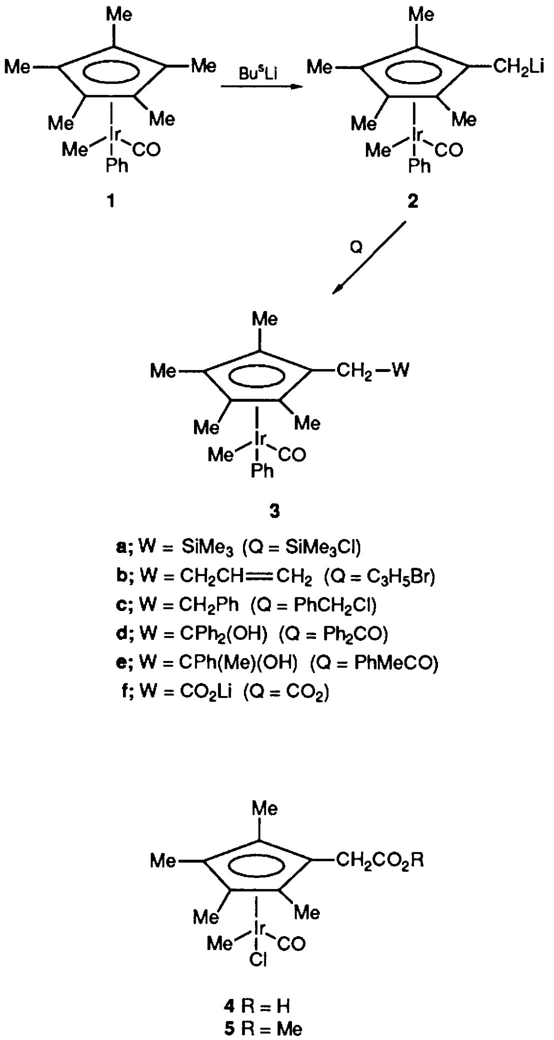
† All new complexes gave satisfactory microanalyses and were characterised by IR, ^1H and ^{13}C NMR spectroscopy.

‡ *Note added in proof:* Single crystal X-ray structure determinations have been completed on **3d** and **4** and will be reported in the full paper.



a; W = SiMe$_3$ (Q = SiMe$_3$Cl)
b; W = CH$_2$CH=CH$_2$ (Q = C$_3$H$_5$Br)
c; W = CH$_2$Ph (Q = PhCH$_2$Cl)
d; W = CPh$_2$(OH) (Q = Ph$_2$CO)
e; W = CPh(Me)(OH) (Q = PhMeCO)
f; W = CO$_2$Li (Q = CO$_2$)

4 R = H
5 R = Me

Scheme 1

ν(CO) 1981 (vs) cm^{-1}]. The ^{1}H NMR resonances were also rather broad, suggesting some dynamic process. Reaction of this material with HCl gas in CH$_2$Cl$_2$, did not give the anticipated [(C$_5$Me$_4$CH$_2$CO$_2$H)Ir(CO)(Me)(Ph)]; instead hydrolysis was accompanied by cleavage of the Ir–Ph bond and the chloromethyl carbonyl acid **4**‡ [ν(CO$_2$) 1707 (vs); ν(CO) 1981 (vs) cm^{-1}] was obtained in 87% yield overall. The carboxylic acid **4** showed a pK_a of 4.65 in ethanol–water (1 : 1). This is significantly stronger than uncomplexed benzoic (pK_a 5.54) or phenylacetic acid (pK_a 5.59) under the same conditions, and is close to the value reported for the chromium tricarbonyl complex of benzoic acid (pK_a 4.52),[7] indicating that Ir^{III} acts in a comparable electron-withdrawing sense. The acid **4** was readily esterified using dicyclohexylcarbodiimide as a promoter, to give the methyl ester **5** [ν(CO$_2$) 1727 (vs), ν(CO) 2015 (vs) cm^{-1}].

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