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Surprisingly facile decomposition of the dication $[(C_5Me_5)Ir(MeO-C_6H_4-CH_2CO_2\overline{NCOCH_2CH_2CO})]^{2+}$: a metal-mediated Hunsdiecker reaction of a succinimidyl ester?

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Abstract

A series of dicationic organoiridium complexes $[Cp^*Ir(arene)]^{2+}$, (**4**, **5** and **6**) have been prepared in which the π-bonded phenyl ring is attached to an alkyl chain terminated by a succinimidyl ester, thus forming Bolton–Hunter reagents for protein labelling. In solution, the benzyl derivative, **4**, underwent facile decomposition. Loss of the succinimidyl moiety followed by decarboxylation led to $[Cp^*Ir(\eta\text{-MeO-}C_6H_4\text{-Me})][BF_4]_2$ (**7**). This product was characterized spectroscopically and by X-ray crystallography. Compound **7** crystallizes in the space group $P2_1/a$ with $a = 13.567(5)$ Å, $b = 17.664(1)$ Å, $c = 9.044(5)$ Å, $\beta = 90.15°$, $V = 2167$ Å^3 and $Z = 4$. A rationale for this surprisingly facile decomposition invokes stabilization of the intermediate benzyl radical by the iridium.

Keywords: Iridium; Hunsdiecker reaction; X-ray structure

1. Introduction

The use of triflate or tetrafluoroborate salts of $[Cp^*M]^{2+}$, where M = Rh or Ir, as organometallic synthons which form complexes with amino acids, or even peptides, has been discussed by Beck et al. [1]. More recently, $[Cp^*Rh(H_2O)_n][CF_3SO_3]_2$ has been reported to facilitate the manipulation of nucleosides in aqueous solution. For example, the aquated rhodium triflate complex formed a stable conjugate with 9-methyladenines. Moreover, the presence of the organometallic moiety '$[Cp^*Rh]$' helped to bring about crystallization of the modified nucleobase [2].

In connection with our programme on the labelling of proteins with organometallic markers, we chose to use the ligands **1–3** (Scheme 1) to prepare a series of $[(C_5Me_5)Ir(arene)]^{2+}$ dications, **4–6**, in which the arene carried an alkyl chain terminated by a succinimidyl ester moiety. Molecules **4**, **5** and **6** may be regarded as Bolton–Hunter reagents [3] in which the aryl ring bears a (pentamethylcyclopentadienyl)iridium moiety. Although the unbound arenes posed no special isolation problems, the organoiridium derivatives showed signs of decomposition, even in the solid state. In particular, the benzyl complex, **4**, underwent facile decomposition in acetone solution at room temperature to yield a brown material. We describe here the characterization of this decomposition product, **7**, and propose a mechanistic rationale to account for these observations.

2. Results and discussion

The use of succinimidyl esters for the selective labelling of amino acids (lysines) in peptide chains has proved to be a valuable method to assay the number of such amino acids which are exposed and available for reaction [4]. As shown in Scheme 1, esters **1–3** were prepared by treatment of the appropriate carboxylic

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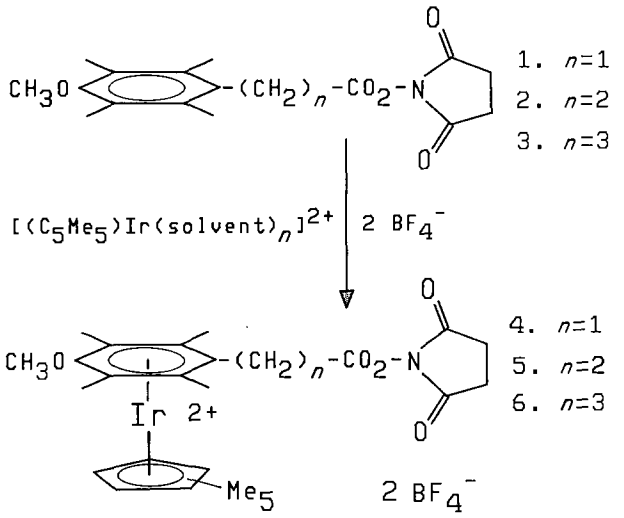


Scheme 1. Synthesis of iridium complexes **4–6**.

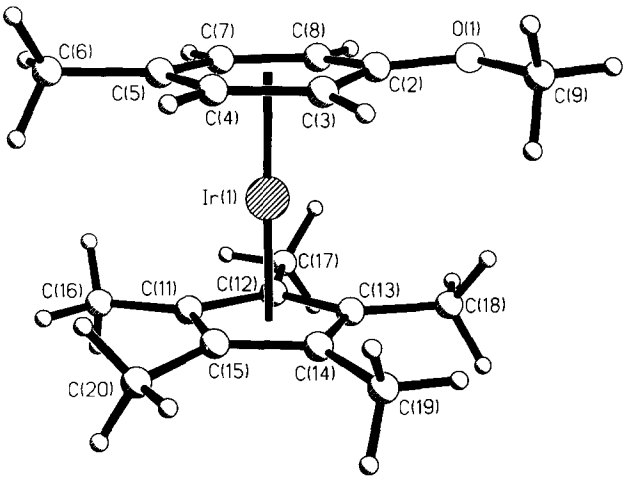


Fig. 1. X-Ray crystal structure of the cation $[(C_5Me_5)Ir(MeOC_6H_4Me)]^{2+}$ (**7**) showing the atom numbering.

acids with *N*-hydroxysuccinimide. Subsequent reaction with $[Cp^*Ir(solvent)_n][BF_4]_2$ [5] prepared in situ from $[\{Cp^*IrCl_2\}_2]$ and AgX (where $X = BF_4$ or CF_3SO_3), yields the desired dicationic iridium complexes, **4–6**. The starting material, $[\{Cp^*IrCl_2\}_2]$, was prepared in 93% yield via a modified procedure, by heating $[\{(COD)IrCl\}_2]$ with C_5Me_5H in methanol under reflux in the presence of concentrated HCl for only 2 h. These organoiridium systems are readily characterized by their ^1H and ^{13}C NMR spectra and no unusual features are evident.

However, after several hours in acetone solution at room temperature, or several days in the solid state, the benzyl derivative, **4**, showed clear signs of decomposition. The initially yellow-orange solution gradually became orange-brown and the NMR spectra revealed new resonances and loss of the resonances assigned to **4**. After separation and purification, the spectra of the decomposition product, **7**, indicated the loss of the succinimidyl ester unit and the appearance of an aromatic methyl group.

The identity of **7** was confirmed by an X-ray crystallographic structural determination; a view of the cation appears as Fig. 1, and crystallographic data are collected in Tables 1–3. The average iridium–C(cyclopentadienyl) and iridium–C(arene) distances are 2.17 Å and 2.25 Å, respectively.

Perhaps the closest analogue to **7** which has been characterized by X-ray crystallography is the dication $[(C_5Me_5)Rh(C_6H_5NHMe)]^{2+}$ (**8**) in which the metal–carbon distances are those observed in the iridium complex **7**. Moreover, in **7**, the Ir–C(OMe) distance (2.35 Å) is markedly longer than are the bonds to its arene ring partners. An analogous situation has been noted in $[(C_5Me_5)Rh(C_6H_5NHMe)]^{2+}$ (**8**) where the Rh–C(NHMe) distance is 2.36 Å [6]. Maitlis has interpreted this in terms of a distortion from η^6-benzenoid geometry, **8′**, towards a 6-imino-1-5-η-cyclohexadienyl structure, **8″**. This gains support from the relatively high barrier to rotation about the C–N bond, which again indicates some degree of carbon–nitrogen multiple-bond character [6].

Table 1
Crystallographic data

Chemical formula	$[IrC_{13}H_{15}O](BF_4)_2$
Molecular weight (g mol^{-1})	623.2
Crystal system	monoclinic
Space group	$P2_1/a$
Z	4
a, Å	13.567(5)
b, Å	17.664(1)
c, Å	9.044(5)
β, deg	90.15(1)
V, Å^3	2167
$F(000)$	1040
ρ (calcd), g·cm^{-3}	1.91
μ (Mo Kα) cm^{-1}	62.08
Cryst. size, mm^3	0.16×0.28×0.36
Diffractometer	Philips PW 1100
Monochromator	graphite
Radiation Mo Kα (0.71070)	
Temperature°C	20
Scan type	$\omega/2\theta$
Scan range θ, deg	1.2 + 0.34 tan θ
2θ range, deg	3–50
Reflctn collected	3779
Reflctn used (criteria)	1758 ($I > 3\sigma(I)$)
R	0.059
R_w [a]	0.066
Absorption correction [b]	min. 0.80, max. 1.14
Secondary ext. 10^6	5.7
Weighting scheme	unit weights
rms (shift/e.s.d) (last ref.)	0.44
l.s. parameters	217

[a] $R_w = [\Sigma_i W_i(F_o - F_o)^2/\Sigma_i W_i F_o^2]^{1/2}$.
[b] Difabs: N. Walker and D. Stuart, *Acta Cryst.*, *A 39* (1983) 159.

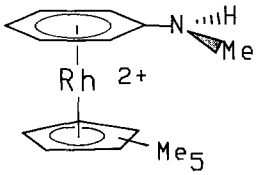
Table 2
Interatomic distances (Å) for $Ir(C_5H_5)(CH_3O\text{-}Ph\text{-}CH_3)$, $2BF_4$

IR(1)–C(2)	2.35(2)	IR(1)–C(3)	2.23(2)
IR(1)–C(4)	2.21(2)	IR(1)–C(5)	2.27(3)
IR(1)–C(7)	2.20(2)	IR(1)–C(8)	2.24(3)
IR(1)–C(11)	2.17(3)	IR(1)–C(12)	2.16(3)
IR(1)–C(13)	2.16(3)	IR(1)–C(14)	2.19(2)
IR(1)–C(15)	2.15(3)	O(1)–C(2)	1.29(3)
O(1)–C(9)	1.42(3)	C(2)–C(3)	1.38(4)
C(2)–C(8)	1.44(4)	C(3)–C(4)	1.42(4)
C(4)–C(5)	1.42(4)	C(5)–C(6)	1.51(5)
C(5)–C(7)	1.41(4)	C(7)–C(8)	1.39(4)
C(11)–C(12)	1.43(4)	C(11)–C(15)	1.45(4)
C(11)–C(16)	1.47(4)	C(12)–C(13)	1.42(4)
C(12)–C(17)	1.55(4)	C(13)–C(14)	1.42(4)
C(13)–C(18)	1.49(4)	C(14)–C(15)	1.41(4)
C(14)–C(19)	1.49(4)	C(15)–C(20)	1.48(4)

Table 3
Main bond angles (deg) for $[C_5Me_5Ir(MeO\text{-}C_6H_4\text{-}Me)][BF_4]_2$

C(3)–Ir(1)–C(2)	35.0(9)	C(4)–Ir(1)–C(2)	64.5(11)
C(4)–Ir(1)–C(3)	37.2(10)	C(5)–Ir(1)–C(2)	78.2(12)
C(5)–Ir(1)–C(3)	67.4(12)	C(5)–Ir(1)–C(4)	36.8(10)
C(7)–Ir(1)–C(2)	65.7(11)	C(7)–Ir(1)–C(3)	77.8(11)
C(7)–Ir(1)–C(4)	65.2(10)	C(7)–Ir(1)–C(5)	36.8(10)
C(8)–Ir(1)–C(2)	36.6(10)	C(8)–Ir(1)–C(3)	64.9(10)
C(8)–Ir(1)–C(4)	76.4(10)	C(8)–Ir(1)–C(5)	66.0(11)
C(8)–Ir(1)–C(7)	36.3(10)	C(11)–Ir(1)–C(2)	166.9(10)
C(11)–Ir(1)–C(3)	158.0(11)	C(11)–Ir(1)–C(4)	126.8(12)
C(11)–Ir(1)–C(5)	107.2(13)	C(11)–Ir(1)–C(7)	111.3(12)
C(11)–Ir(1)–C(8)	134.1(11)	C(12)–Ir(1)–C(2)	129.1(12)
C(12)–Ir(1)–C(3)	158.9(12)	C(12)–Ir(1)–C(4)	163.9(12)
C(12)–Ir(1)–C(5)	130.7(12)	C(12)–Ir(1)–C(7)	110.1(11)
C(12)–Ir(1)–C(8)	109.4(11)	C(13)–Ir(1)–C(2)	107.8(11)
C(13)–Ir(1)–C(3)	122.9(12)	C(13)–Ir(1)–C(4)	154.1(12)
C(13)–Ir(1)–C(5)	169.0(13)	C(13)–Ir(1)–C(7)	136.6(12)
C(13)–Ir(1)–C(8)	113.0(11)	C(14)–Ir(1)–C(2)	116.7(11)
C(14)–Ir(1)–C(3)	107.3(11)	C(14)–Ir(1)–C(4)	120.6(11)
C(14)–Ir(1)–C(5)	147.6(12)	C(14)–Ir(1)–C(7)	174.2(11)
C(14)–Ir(1)–C(8)	142.9(11)	C(15)–Ir(1)–C(2)	149.3(11)
C(15)–Ir(1)–C(3)	122.1(10)	C(15)–Ir(1)–C(4)	109.2(10)
C(15)–Ir(1)–C(5)	115.8(12)	C(15)–Ir(1)–C(7)	141.7(12)
C(15)–Ir(1)–C(8)	173.0(11)	C(12)–Ir(1)–C(11)	38.6(11)
C(13)–Ir(1)–C(11)	65.0(12)	C(13)–Ir(1)–C(12)	38.4(10)
C(14)–Ir(1)–C(11)	65.1(12)	C(14)–Ir(1)–C(12)	64.2(10)
C(14)–Ir(1)–C(13)	38.2(10)	C(15)–Ir(1)–C(11)	39.2(11)
C(15)–Ir(1)–C(12)	64.1(11)	C(15)–Ir(1)–C(13)	63.7(11)
C(15)–Ir(1)–C(14)	37.9(9)		

The longer chain systems **5** and **6** also undergo decomposition, but in these cases the reaction is considerably slower (weeks) and the products are less amenable to spectroscopic or crystallographic characterization.



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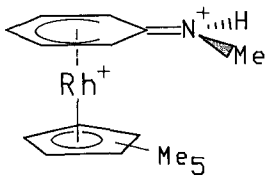

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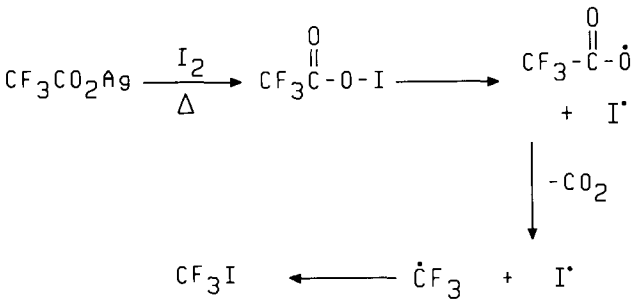
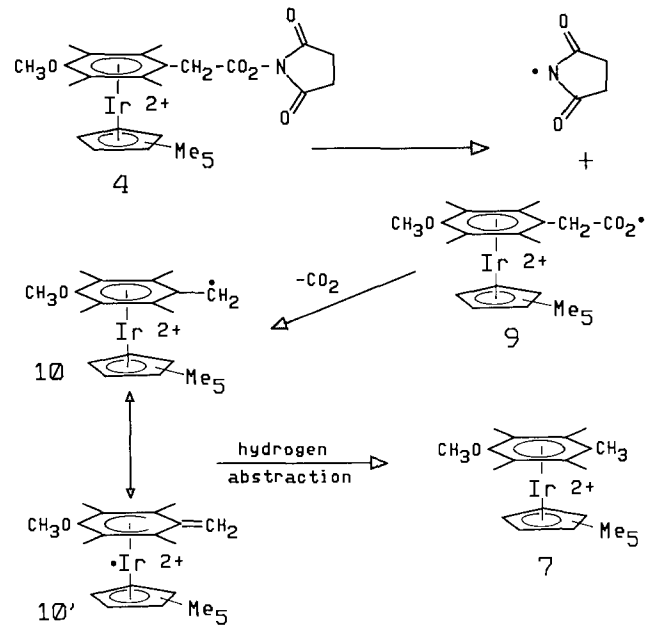


Scheme 2. Mechanism of the Hunsdiecker reaction.

The remarkably smooth transformation of **4** into **7** poses interesting mechanistic questions and one must search for analogues in the organic domain. We note that the Hunsdiecker reaction, a radical-induced decarboxylation process, proceeds via a hypohalite intermediate, as exemplified in Scheme 2 [7]. The relatively weak oxygen–halogen bond breaks homolytically to yield a carboxylate radical which, after extrusion of CO_2, couples with the halogen atom. The similarity with the conversion of **4** to **7** is apparent. The O–N link in **4** can break homolytically to produce the succinimidyl radical (a well-known intermediate in radical chain brominations) and the carboxylate radical **9**. Subsequent loss of CO_2 from **9** yields the benzyl system **10** which can simply abstract a hydrogen atom from the solvent, as in Scheme 3.

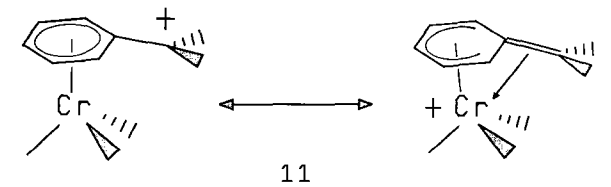
The immediate question which arises is the role of the iridium, which facilitates a reaction that the unbound arene does not readily undergo. Moreover, any proposal must account for the particularly facile reac-



Scheme 3. Proposed Hunsdiecker-type route to $[(C_5Me_5)Ir(MeOC_6H_4Me)]^{2+}$ (7).

tion of the benzyl complex **4** relative to the behaviour of **5** and **6**. These data are reminiscent of other metal–benzyl systems in which short-lived intermediates are stabilized by direct or indirect charge delocalization onto the metal. Typically, the [(benzyl)Cr-$(CO)_3$]$^+$ cation **11** [8] and metal–fluorenide system **12** [9] can be isolated and characterized by spectroscopic or crystallographic techniques. One can readily envisage the stabilization of the iridium-benzyl radical, **10**, via delocalization of electron density onto the metal, as in **10′**. Such a metal-stabilized radical could adopt a 17-electron or a 19-electron configuration, depending on whether the exocyclic methylene interacts directly with the metal or not [10]. An EHMO calculation on the model system [(η-$C_6H_5CH_2$)Ir(C_5H_5)]$^{2+}$ yields an energy-minimized structure in which the exocyclic methylene unit remains in the plane of the aryl ring. We note that a number of Rh and Ir complexes of cyclohexadienyl systems bearing an exocyclic double bond have been reported, including [$(Ph_3P)_2$Rh(η^5-2,6-^{t}Bu$_2$-4-Me-C_6H_2O)] [11], [Cp*Rh(η^5-estradienonyl)][BF_4] [12], and [Cp*Ir(η^5-C_6H_5O)][PF_6] [13].

The mechanisms of decarboxylation of organometallic esters have been comprehensively reviewed [14], and generally proceed via radical or anionic intermediates. Loss of CO_2 is particularly favoured when the metal can intervene directly in the decarboxylation step. The metal-mediated decarboxylation of [(C_6H_6)Cr(C_6F_5-CO_2Et)] to yield [(C_6H_6)Cr(C_6F_5H)] exemplifies such a reaction, in which an ester, **13**, is readily transformed into the corresponding hydrocarbon, **14**. This reaction appears to proceed via an anionic rather than a radical intermediate [15].



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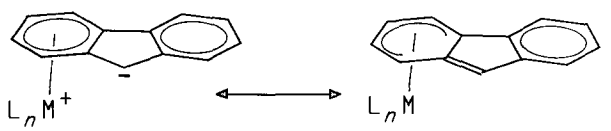
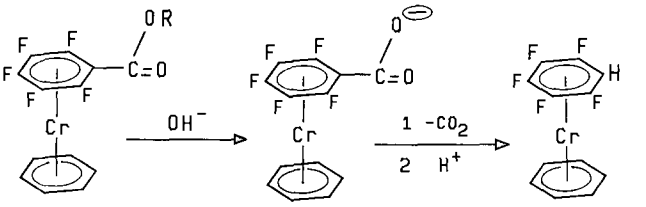


12 ML_n = (C_5H_5)Fe or Mn(CO)$_3$



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The instability of the benzyl complex **4** represented a major obstacle with respect to its reactivity towards amines. However, the homologous phenethyl complex **5** reacts rapidly with the ethyl ester of β-alanine in THF to give a mixture of products. The ^{1}H NMR spectrum of the crude mixture reveals the conjugate product which possesses a primary amide linkage. These data suggest that the dicationic compounds **4–6** are very reactive compared to the analogous neutral species, **1–3** [16], but are less selective towards amines or amino acids with respect to formation of peptide links. It appears that the presence of the dicationic fragment [Cp* Ir]$^{2+}$ on the aromatic ring of the succinimidyl esters **4–6** weakens the 'CH_2–O' bond and facilitates its cleavage, affording several side-products in their reactions with amino substrates. To prevent this, we are focussing our efforts on the syntheses and chemistry of mono-cationic ruthenium analogues as well as neutral organometallic species bearing a succinimidyl leaving group. These studies will be the subject of future reports.

3. Experimental section

All manipulations were carried out under argon using Schlenk techniques. Solvents were purified and dried by conventional distillation techniques prior to use. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM 250 instrument operating at 250 MHz and 62.86 MHz, respectively. IR spectra were obtained on a FT-Bomem 100 instrument. Elemental analyses were performed by the Microanalytical Laboratory of the CNRS ICSN, Gif-sur-Yvette.

3.1. Preparation of N-succinimidyl-3-(4-hydroxyphenyl) propionate (2)

Following the general procedure of Anderson [17], *N*-hydroxysuccinimide (0.6 g, 5 mmol) was added to 3-(4-methoxyphenyl)propionic acid (0.9 g, 5 mmol) in THF (5 cm^3) and the reaction mixture was stirred at −18°C. Dicyclohexylcarbodiimide (1.2 g, 6 mmol) was added and the mixture was stirred for 2 h at −18°C and then at room temperature overnight. The suspension which formed was treated with acetic acid (0.12 cm^3) and stirred for a further 1 h. The suspension was diluted with ethyl acetate (10 cm^3) and filtered. The

filtrate was evaporated to dryness to give a colourless product which was recrystallized from THF/Et_2O at low temperature to yield colourless needles (1.2 g, 0.43 mmol; 86%). ^1H NMR (250 MHz, $CDCl_3$) δ 7.08 (d, $J = 4$ Hz, 2H, phenyl H's), 6.82 (d, $J = 4$ Hz, 2H, phenyl H's), 3.79 (s, 3H, CH_3O), 3.00 (m, 4H, $-CH_2-CH_2-$), 2.84 (s, 4H, succinimidyl H's). $^{13}C\{^1H\}$ NMR (62.86 MHz, $CDCl_3$) 169.1 (CO), 167.9 (CO), 158.4, 131.2 (phenyl C's), 129.2, 114.1 (phenyl CH's), 55.2 (CH_3O), 32.9, 29.6 (CH_2-CH_2), 25.5 (CH_2-CH_2 succinimidyl).

3.2. Preparation of N-succinimidyl-3-(4-hydroxyphenyl) ethanoate (1)

Analogously to the preparation of **2**, *N*-succinimidyl-3-(4-methoxyphenyl)ethanoate was prepared in 84% yield from *N*-hydroxysuccinimide and 3-(4-methoxyphenyl)ethanoic acid. Recrystallization from THF/pentane gave colourless fluffy crystals. ^1H NMR (250 MHz, acetone-d_6) δ 7.30 (d, $J = 4$ Hz, 2H, phenyl H's), 6.92 (d, $J = 4$ Hz, 2H, phenyl H's), 3.95 (s, 2H CH_2), 3.79 (s, 3H, CH_3O), 2.87 (s, 4H, succinimidyl H's). $^{13}C\{^1H\}$ NMR (62.86 MHz, acetone-d_5) 170.5 (CO), 160.0 (CO), 140.8, 123.4 (phenyl C's), 131.2, 114.7 (phenyl CH's), 62.8 (CH_2), 55.3 (CH_3O), 26.1 (CH_2-CH_2 succinimidyl).

3.3. Preparation of N-succinimidyl-3-(4-hydroxyphenyl) butanoate (3)

Analogously to the preparation of **2**, *N*-succinimidyl-3-(4-methoxyphenyl)butanoate was prepared in 70% yield from *N*-hydroxysuccinimide and 3-(4-methoxyphenyl)butanoic acid. Recrystallization from THF/Et_2O gave colourless microcrystals. ^1H NMR (250 MHz, $CDCl_3$), δ 7.11 (d, $J = 4$ Hz, 2H, phenyl H's), 6.84 (d, $J = 4$ Hz, 2H, phenyl H's), 3.79 (s, 3H, CH_3O), 2.84 (s, 4H, succinimidyl H's), 2.68 (t, 2H CH_2), 2.59 (t, 2H CH_2), 2.05 (m, 2H CH_2). $^{13}C\{^1H\}$ NMR (62.86 MHz, $CDCl_3$) 169.2 (CO), 168.5 (CO), 158.0, 132.6 (phenyl C's), 129.4, 113.9 (phenyl CH's), 55.2 (CH_3O), 33.6, 30.0, 26.4 (CH_2's), 26.1 (CH_2-CH_2 succinimidyl).

3.4. Preparation of (pentamethylcyclopentadienyl)η^6-N-succinimidyl-3-(4-hydroxyphenyl)ethanoate]indium (4)

Following the general synthetic procedure of Maitlis [5], $[\{Cp^*IrCl_2\}_2]$ (133 mg, 0.17 mmol) dissolved in 50:50 CH_2Cl_2/THF (10 cm^3) was treated with $AgBF_4$ (150 mg, 0.76 mmol) in an acetone/THF mixture. The solution turned orange and a white precipitate of AgCl appeared. After stirring for a further 15 min, the orange solution of $[Cp^*Ir(solvent)_n][BF_4]_2$ was treated with the succinimidyl ester, **1**, (90 mg, 0.34 mmol) in THF (8 cm^3), and the reaction mixture was stirred under argon. Best yields of **4** were obtained after stirring for 4–5 h. Longer reaction times resulted in decomposition and **7**, as the major product. The mixture was concentrated under vacuum and subsequent addition of diethyl ether afforded a light yellow precipitate of unreacted $[Cp^*Ir(THF)_n]^{2+}$ salt. The supernatant liquid was evaporated to dryness and then washed with several times with diethyl ether to yield a light yellow oil which solidified upon washing with pentane to yield **4** (75 mg, 0.104 mmol; 30%). ^1H NMR (250 MHz, acetone-d_6) δ 7.76 (d, $J = 3$ Hz, 2H, phenyl H's), 7.66 (d, $J = 3$ Hz, 2H, phenyl H's), 4.54 (s, 2H, CH_2), 3.94 (s, 3H, CH_3O), 2.91 (s, 4H, CH_2-CH_2 succinimidyl), 2.44 (s, 15H, Me's).

3.5. Preparation of (methylcyclopentadienyl)η^6-N-succinimidyl-3(4-hydroxyphenyl)propionate]indium (5)

Analogously to the synthesis of **4**, the propionate complex **5** was obtained in 60% yield as off-white microcrystals. ^1H NMR (250 MHz, acetone-d_6) δ 7.63 (d, $J = 3$ Hz, 2H, phenyl H's), 7.56 (d, $J = 3$ Hz, 2H, phenyl H's), 4.23 (s, 3H, CH_3O), 3.2 (dt, 4H, CH_2-CH_2), 2.88 (s, 4H, CH_2-CH_2 succinimidyl), 2.47 (s, 15H, Me's). $^{13}C\{^1H\}$ NMR (62.86 MHz, CD_3CN) δ 170.9 (CO), 168.6 (CO), 145.1, 110.1 (phenyl C's), 106.15 (cyclopentadienyl C's), 98.0, 84.6 (phenyl CH's), 60.9 (CH_3O), 31.5, 26.8 (CH_2's), 26.4 (CH_2-CH_2 succinimidyl), 10.3 (Me's). Analysis. Found: C, 37.54; H, 3.92; N, 1.60; $C_{24}H_{30}B_2F_8IrNO_5$ calcd.: C, 37.02; H, 3.86; N, 1.8%.

3.6. Preparation of (pentamethylcyclopentadienyl)[η^5-N-succinimidyl-3-(4-hydroxyphenyl)butanoate]iridium (6)

Analogously to the syntheses of **4** and **5**, the butanoate complex **6** was obtained in 50% yield as off-white microcrystals. ^1H NMR (250 MHz, acetone-d_6) δ 7.60 (d, $J = 3$ Hz, 2H, phenyl H's), 7.46 (d, $J = 3$ Hz, 2H, phenyl H's), 4.25 (s, 3H, CH_3O), 3.60 (m, 2H, CH_2), 2.93 (m, 2H, CH_2), 2.89 (s, 4H, CH_2-CH_2 succinimidyl), 2.84 (m, 2H, CH_2), 2.43 (s, 15H, Me's). $^{13}C\{^1H\}$ NMR (62.86 MHz, acetone-d_6) δ 170.7 (CO), 169.1 (CO), 144.9, 111.7 (phenyl C's), 105.7 (cyclopentadienyl C's), 97.7, 84.9 (phenyl CH's), 60.3 (CH_3O), 31.0, (CH_2's; other methylene peaks obscured by solvent), 26.3 (CH_2-CH_2 succinimidyl), 10.2 (Me's).

3.7. Preparation of [C_5Me_5]Ir(η^6-MeO-C_6H_4-Me)]-[BF_4]$_2$ (7)

The salt **7** was obtained, initially accidently but subsequently reproducibly, by slow decomposition of **4** in an acetone/THF mixture but it was also formulated

during the preparation of **4**. A rapid and convenient route to **7** involves heating the light orange solution of **4** under reflux for 2–3 h, during which time the mixture turns orange-brown. After concentration of the solution under vacuum, addition of diethyl ether afforded an orange-brown precipitate essentially quantitatively. Recrystallization from acetone/Et_2O yielded crystals of X-ray quality. ^1H NMR (250 MHz, CD_3CN) δ 7.06 (d, $J = 3$ Hz, 2H, phenyl H's), 6.98 (d, $J = 3$ Hz, 2H, phenyl H's), 4.03 (s, 3H, CH_3O), 2.42 (s, 3H, CH_3), 2.22 (s, 15H, Me's). $^{13}C\{^1H\}$ NMR (62.86 MHz, CD_3CN) δ 144.2, 110.7 (phenyl-C's), 105.7 (cyclopentadienyl C's), 97.7, 84.3 (phenyl CH's), 60.7, (CH_3O) 17.4 (CH_3,), 10.2 (Me's).

3.8. X-ray crystallography

Suitable crystals of $[(C_5Me_5)Ir(MeO-C_6H_4-Me)][BF_4]_2$, (**7**) were obtained by recrystallization from acetone/Et_2O. Crystallographic data are collected in Table 1. Accurate cell dimensions and orientation matrices were obtained by least-squares refinement of 25 accurately centred reflections on a Nonius CAD4 diffractometer equipped with graphite-monochromated Mo Kα radiation. No significant variations were observed in the two check reflections during data collection. The data were corrected for Lorentz and polarization effects; an empirical absorption correction (DIFABS) [18] was applied. Computations were performed by using CRYSTALS [19] modified locally for a Microvax II computer. Scattering factors and corrections for anomalous absorption were taken from ref. [20]. The structure was solved by direct methods (SHELXS) [21] and refined by full-matrix least-squares with anisotropic thermal parameters for all non-hydrogen atoms. All hydrogen atoms were then located on a difference Fourier map and their coordinates refined with an isotropic thermal parameter. The structure was refined to $R = 0.059$ and $R_w = 0.066$ with use of 1758 reflections for 217 least-squares parameters. Final atomic coordinates and selected bond distances are listed in Tables 2 and 3. Full lists of parameters have been deposited with the Cambridge Crystallographic Data Centre. Anisotropic temperature factors, and observed and calculated structure factor amplitudes are also available from the authors.

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