Ring-methyl Activation in Pentamethylcyclopentadienyliridium Complexes. Part 2.[1] Synthesis of C_5Me_4(functionalized alkyl) Complexes and Crystal Structures of $[(C_5Me_4CH_2CPh_2OH)IrMe(CO)Ph]$ and $[(C_5Me_4CH_2CO_2H)IrMe(CO)Cl]$ †

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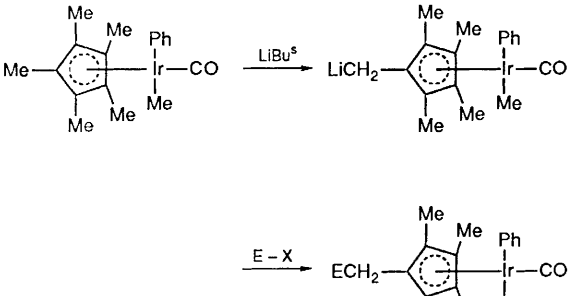
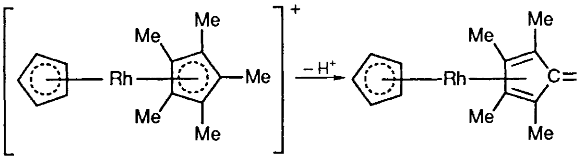
Reaction of $[(C_5Me_5)IrMe(CO)Ph]$ **1** with *sec*-butyllithium gives a lithio complex, presumably $Li[(C_5Me_4CH_2)IrMe(CO)Ph]$ **2**, which reacts with PhCOR to give the appropriately substituted $[\{C_5Me_4CH_2CPh(OH)R\}IrMe(CO)Ph]$ **3a** (R = Me) and **3b** (R = Ph). Hydrogen chloride cleaved the Ir–Ph bonds in complexes **3a** and **3b** to give first $[\{C_5Me_4CH_2CPh(OH)R\}IrMe(CO)Cl]$ **4**, which reacted further with HCl to give $[\{C_5Me_4CH_2CPh(Me)Cl\}Ir(CO)Cl_2]$ **5**, from **4a**, and $[(C_5Me_4CH{=}CPh_2)Ir(CO)Cl_2]$ **6**, from **4b**. Complex **2** also reacted with PhCN and with CO_2 to give, after work-up, the substituted acetophenone and the substituted acetic acid complexes $[(C_5Me_4CH_2COPh)IrMe(CO)Ph]$ **7** and $[(C_5Me_4CH_2CO_2H)IrMe(CO)Cl]$ **8**, respectively. Complex **8** was converted by further HCl into $[(C_5Me_4CH_2CO_2H)Ir(CO)Cl_2]$ **9**, or esterified (ROH, base and dicyclohexylcarbodiimide) to give $[(C_5Me_4CH_2CO_2R)IrMe(CO)Cl]$ **10a** (R = Me) or **10b** (R = 1*R*,2*S*,5*R*-menthyl). Complex **9** was also esterified (EtOH, HCl) to give $[(C_5Me_4CH_2CO_2Et)Ir(CO)Cl_2]$ **11**. Reaction of the complex $[\{C_5Me_4(CH_2SiMe_3)\}IrMe(CO)Ph]$ **12** with *sec*-butyllithium followed by CO_2 gave $[\{C_5Me_3(CH_2CO_2H)(CH_2SiMe_3)\}IrMe(CO)Cl]$ **13**. X-Ray structure determinations of complexes **3b** and **8** were carried out: **3b** shows no hydrogen bonding, but molecules of **8** are linked across a crystallographic inversion centre by pairs of strong hydrogen bonds between the carboxylic acid residues.

We recently reported that the pentamethylcyclopentadienyliridium complex $[(C_5Me_5)IrMe(CO)Ph]$ **1** reacts readily with *sec*-butyllithium in tetrahydrofuran at low temperature to give a metallated species, presumably $Li[(C_5Me_4CH_2)IrMe(CO)Ph]$ **2**, which in turn reacts with organic and inorganic halides, E–X, to give complexes in which one (or more) ring methyl has been replaced by CH_2E [E = alkyl, $CH_2{=}CHCH_2$, $PhCH_2$, Me_3Si, *etc.* equation (1)].[1] Although the lithio-complex **2** has not yet been characterised, we have been able to isolate and characterise a related rhodium species, equation (2).[2] The intermediate lithio-compound **2** reacts readily with a number of compounds containing oxy-functions. This paper describes such reactions with phenyl ketones (PhCOR), carbon dioxide, and a closely related reaction with benzonitrile. A preliminary communication on part of this work has appeared.[3]



(1)



$$\xrightarrow{E-X} [(C_5Me_4CH_2E)Rh(C_5H_5)]X \qquad (2)$$

Results and Discussion

Reactions with Ketones.—The lithio-complex **2** reacted readily with ketones; the cleanest products were obtained with phenyl ketones, which gave the tertiary alcohols $[\{C_5Me_4CH_2CPh(OH)R\}IrMe(CO)Ph]$ **3a** (R = Me) and **3b** (R = Ph) in 79 and 77% yield respectively on work-up. These complexes were identified spectroscopically (Tables 1–3) and also by an X-ray structure determination of **3b**.

The ^1H and the ^{13}C NMR spectra showed four signals for the C_5Me_5 methyls in the diphenyl carbinol complex **3b**, as expected for a diastereotopic system. However, the C_5Me_4 gave eight methyl signals (two coincident) and ten ring-carbon signals for the phenyl methyl carbinol complex **3a**, indicating the presence of diastereoisomers, and reflected the presence of two chiral centres, the iridium and the CPh(Me)OH.

An X-ray determination showed (Fig. 1) that the molecule **3b** comprised an iridium η^5 co-ordinated to a pentasubstituted cyclopentadienyl [root-mean-square (r.m.s.) deviation 0.015 Å, perpendicular displacement of metal 1.920 Å]. Three of the four methyl ring substituents are displaced above the ring plane (away from the metal) by up to 0.16 Å, but methyl C(23) is in the mean plane. The fifth substituent is CH_2CPh_2OH, the attached carbon of which is displaced 0.03 Å from the mean ring plane away from the metal. The two phenyls are each planar (r.m.s.

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† Carbonyl[η^5-(2-hydroxy-2,2-diphenylethyl)tetramethylcyclopentadienyl]methylphenyliridium and carbonyl[η^5-(carboxymethyl)tetraethylcyclopentadienyl]chloromethyliridium.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

deviations 0.013 and 0.032 Å), are mutually inclined at 95°, and are inclined at 47° and 101° to the C_5 ring plane. The OH is not hydrogen bonded and there are no noteworthy intermolecular contacts.

The three basal ligands attached to the iridium are phenyl (r.m.s. deviation 0.010 Å), carbonyl and methyl. The carbonyl and the methyl were found to be equally disordered between their sites. The bond angles between the basal ligands are all fairly close to 90° for both conformations of the disorder components; the Ir–C(phenyl) is 2.091 Å.

The presence of the OH in the ^{1}H NMR spectrum (δ 2.05) as a singlet for **3b** (and probably a badly obscured multiplet at δ 1.64 for **3a**) confirms the absence of hydrogen bonding. Further, the complexes show sharp ν(OH) in the IR spectra, at 3555 for **3a** and 3598 cm^{-1} for **3b**. The ν(CO), at 1994 cm^{-1} for both, is very similar to that for the unsubstituted complex (1988 cm^{-1})[4] and shows that no significant electronic changes have taken place at the metal.

Table 1 Microanalytical[a] and IR data

	IR (cm^{-1})			Microanalysis (%)			
Complex	ν(OH)[b]	ν(CO)[c]	$\nu(CO_2)$[d]	C	H	Cl	Yield (%)
3a	3555	1994[e]		55.7	5.8		79
				(55.0)	(5.5)		
3b	3598	1994[e]		59.0	5.1		77
				(59.1)	(5.3)		
4a	3418	2011		45.9	5.0	6.5	73
				(45.7)	(5.0)	(6.7)	
4b	3423[d]	2010		51.3	4.6	6.4	72
				(51.1)	(4.8)	(6.0)	
5		2061		40.9	3.9	19.0	67
				(40.4)	(3.9)	(18.8)	
6		2059		48.5	4.2	11.7	88
				(48.8)	(3.9)	(12.0)	
7		1994[e]		54.7	5.1		48
		1687[b]		(54.4)	(4.9)		
8		2016	1707	34.6	4.0	7.8	92
				(34.7)	(4.0)	(7.9)	
9		2063	1707	30.5	3.1	15.1	94
				(30.6)	(3.2)	(15.1)	
10a		2015	1727	36.4	4.2	7.4	54
				(36.2)	(4.3)	(7.6)	
10b		2014	1734	47.1	5.9	6.0	57
				(47.0)	(6.2)	(6.0)	
11		2062	1732	33.7	4.0	14.2	91
				(33.7)	(3.8)	(14.2)	
13		2013	1731	36.9	4.8	6.8	79
				(36.8)	(5.0)	(6.8)	

[a] Calculated values in parentheses. [b] Nujol mull. [c] In CH_2Cl_2 solution. [d] As KBr disc. [e] Pentane solution.

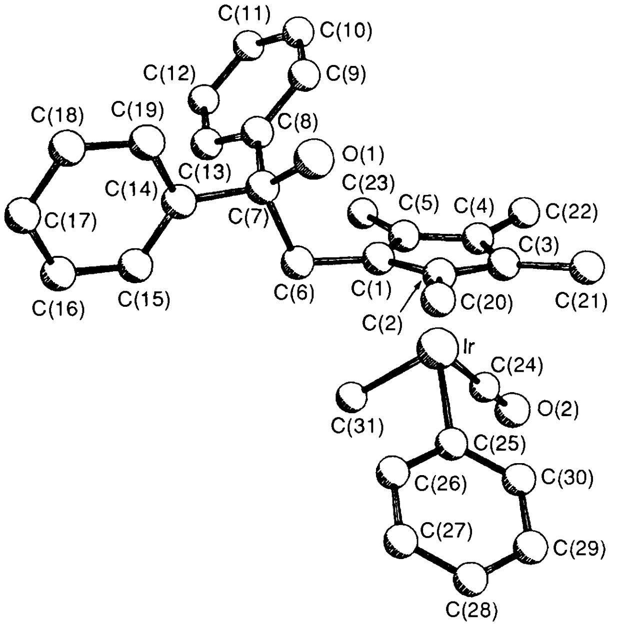


Fig. 1 A view of the structure of $[(C_5Me_4CH_2CPh_2OH)IrMe(CO)Ph]$ **3b** with hydrogens omitted for clarity

Table 2 Proton NMR spectra ($CDCl_3$ solution)

Complex	C_5Me_4	Me–Ir	Ph–Ir	CH_2R	R
3a	1.62 (s, 6 H), 1.66 (s, 3 H), 1.67 (s, 3 H), 1.72 (s, 3 H), 1.73 (s, 3 H), 1.73 (s, 3 H), 1.77 (s, 3 H)	0.61 (s)	6.95 (m) 7.11 (m)	2.63 (m)	Ph, 7.33 (m); Me, 1.28 (s), 1.33 (s); OH, 1.64 (m)
3b	1.24 (s), 1.33 (s), 1.68 (s), 1.70 (s)	0.62 (s)	6.95 (m) 7.13 (m)	3.06 (m)	Ph, 7.27 (m); OH, 2.05 (s)
4a	1.91 (s), 1.89 (s), 1.85 (s), 1.82 (s), 1.74 (s), 1.71 (s), 1.70 (s), 1.69 (s)	1.00 (s) 1.01 (s)		2.66 (m)	Me, 1.20 (s); Ph, 7.34 (m); OH, 1.80 (m)
4b	1.36 (s), 1.39 (s), 1.77 (s), 1.79 (s)	1.03 (s)		3.21 (s)	OH, 2.21 (s, 1 H); Ph, 7.31 (m, 10 H)
5	1.81 (s), 1.92 (s), 1.99 (s), 2.11 (s)			3.01 (m)	Me, 1.17 (s, 6 H); Ph, 7.49 (m, 4 H), 7.34 (m, 6 H)
6*	1.54 (s), 1.82 (s)				CH=, 6.30 (s); Ph, 7.09 (m, 2 H), 7.35 (m, 8 H)
7	1.67 (s), 1.76 (s), 1.82 (s), 1.86 (s)	0.73 (s)	7.00 (m) 7.21 (m)	3.75 (m)	Ph, 7.50 (m, 2 H), 7.61 (m, 1 H), 7.95 (m, 2 H)
8	1.87 (s), 1.89 (s), 1.91 (s), 1.97 (s)	1.10 (s)		3.28 (m)	
9	1.94 (s), 1.95 (s)			3.33 (s)	
10a	1.85 (s), 1.87 (s), 1.88 (s), 1.92 (s)	1.08 (m)		3.21 (m)	OMe, 3.72 (s)
10b	1.85 (s), 1.86 (s), 1.87 (s, 9 H), 1.88 (s), 1.90 (s), 1.91 (s)	1.08 (s)		3.18 (s) 3.18 (m)	Menthyl, C^1H 4.67 [dt, 11 and 4 Hz], C^8H_3, C^9H_3 0.88 (t, 7 Hz), C^7H_3, 0.72 (d, 7 Hz), rest 0.95–2.20
11	1.93 (s), 1.94 (s)			3.27 (s)	OEt, 4.19 (q, 7.5 Hz), 1.29 (t)
13	1.78 (s), 1.84 (s, 6 H), 1.87 (s), 1.90 (s), 1.97 (s)	1.06 (s)		CH_2Si, 1.65 (m); CH_2CO_2H 3.25 (m), 3.29 (m)	Me_3Si; 0.07 (s, 9 H), 0.07 (s, 9 H)

* In CD_2Cl_2 solution.

Table 3 Carbon-13 NMR spectra ($CDCl_3$ solution)

			Ph–Ir						
Complex	C_5Me_4	Me–Ir	C^4	$C^{3,5}$	C^1	$C^{2,6}$	CO	CH_2R	R
3a	8.5, 8.6, 8.7, 9.3, 9.5, 10.1, 10.2, 96.3, 96.4, 98.2, 98.2, 98.4, 98.6, 100.5, 100.6, 101.7, 101.7	−22.0	122.7,	127.9,	130.5,	139.7	172.5	39.4	Me, 29.7, 29.7; COH, 76.0; Ph, 125.2 (C^4), 127.1, 128.2 ($C^{2,3}$), 147.3, 147.4 (C^1)
3b	8.6, 8.7, 9.4, 9.4, 96.2, 98.3, 98.7, 100.9, 101.2	−22.0	122.8,	127.9,	130.6,	139.8	172.5	37.4	COH, 78.9; Ph, 126.7 (C^4), 127.3, 128.1 ($C^{2,3}$), 146.7 (C^1)
4a	8.4, 8.6, 8.6, 8.8, 9.0, 9.1, 10.3, 10.4, 96.7, 96.9, 98.3, 98.4, 98.6, 99.1, 100.0, 100.4, 103.7	−17.1 −17.0					170.5 170.6	39.1 39.2	Me, 30.1, 30.4; COH, 75.7, 75.8; Ph, 125.1, 125.2 (C^4), 127.3, 128.4, 128.6 (C^{2-6}), 146.7, 146.9 (C^1)
4b	8.4, 8.8, 9.5, 9.7, 96.5, 97.6, 98.2, 100.9, 104.6	−17.0					170.7	37.0	COH, 79.1; Ph_2 126.6, 126.7, 127.6, 128.3 (C^{2-4}), 146.3, 146.5 (C^1)
5	9.1, 9.2, 9.7, 11.5, 94.9, 100.3, 100.5, 102.9, 103.0						166.8	39.5	CCl, 75.3; Me, 30.8; Ph, 126.4 (C^4), 128.4, 128.6 ($C^{2,3}$), 143.2 (C^1)
6*	9.2, 10.2						167.3		$C^1H=$, 115.4; $C^2=$, 151.9; Ph, 128.8, 129.0, 129.1, 129.2, 129.4, 130.3 (C^{2-6}); 139.3, 141.6 (C^1)
7	8.7, 8.7, 9.0, 92.8, 98.5, 99.0, 100.9, 101.2	−22.2	122.9,	128.1,	130.1,	139.8	172.5	34.3	COPh, 196.0; Ph, 128.8 (C^3), 133.6 (C^2), 136.1 (C^1), 139.8 (C^4)
8	8.7, 9.0, 9.0, 90.6, 97.8, 98.1, 102.9, 103.7	−17.2					169.7	29.5	CO_2H, 175.1
10a	8.7, 8.9, 8.9, 91.3, 98.2, 98.3, 102.5, 103.4	−17.3					169.9	29.6	OMe, 52.3; CO_2Me, 169.9
10b	8.7, 8.8, 91.6, 98.6, 102.2, 102.5, 102.9, 103.0	−17.5					170.1	30.2	CO_2, 169.3; Menthyl (C^1), 75.6, (C^2) 47.1, (C^3) 23.4, (C^4), 40.8, (C^5) 31.4, (C^6) 34.1, (C^7) 21.9, (C^8) 26.5, (C^9) 16.3, (C^{10}) 20.6
11	9.3, 9.3, 90.6, 99.3, 104.4						165.9	30.0	CH_3, 14.1; OCH_2, 61.9; CO_2, 168.4
13	8.8, 9.2, 9.2, 9.2, 9.6, 9.7, 91.3, 91.5, 92.3, 93.1, 94.0, 97.5, 103.2	−16.6 −16.6					170.1 170.2	CH_2Si, 13.7, 14.0; CH_2CO_2H, 29.5, 29.6	Me_3Si, −0.6; CO_2, 174.7, 175.0

* In CD_2Cl_2.

Table 4 Selected bond lengths (Å) and angles (°) for $[(C_5Me_4CH_2CPh_2OH)IrMe(CO)Ph]$ **3b**

Ir–C(1)	2.272(15)	Ir–C(2)	2.277(14)
Ir–C(3)	2.246(16)	Ir–C(4)	2.263(21)
Ir–C(5)	2.271(23)	Ir–C(25)	2.091(20)
Ir–C(31)	2.032(32)	Ir–C(31a)	2.032(27)
C(24)–Ir–C(31)	90.6(8)	C(31)–Ir–C(25)	83.9(13)
C(24a)–Ir–C(31a)	83.9(9)	C(1)–C(6)–C(7)	115.7(12)
C(24)–Ir–C(25)	90.7(4)	C(6)–C(7)–O(1)	105.7(12)
C(24a)–Ir–C(25)	87.9(4)	C(8)–C(7)–O(1)	109.9(13)
C(31a)–Ir–C(25)	87.7(13)	C(14)–C(7)–O(1)	110.7(11)

When **3a** or **3b** was treated with HCl under very mild conditions the Ir–Ph bond was cleaved to give the corresponding *tert*-alcohol iridium methyl carbonyl chloride complexes, $[\{C_5Me_4CH_2CPh(OH)R\}IrMe(CO)Cl]$ **4a** (R = Me) or **4b** (R = Ph). These complexes also showed similar spectroscopic features in the NMR spectra to those of **3a** or **3b**; for example, **4b** showed four different methyl signals while **4a** showed eight. The value of ν(CO) for the carbonyl chlorides **4a** (2011) and **4b** (2010 cm^{-1}) was somewhat higher, reflecting less back bonding.

We previously noted that prolonged reaction of the complexes $[(C_5Me_4CH_2E)IrMe(CO)Ph]$ (E = hydrocarbyl) with HCl resulted in smooth cleavage first of the Ir–Ph and then of the Ir–Me bond to yield $[(C_5Me_4CH_2E)Ir(CO)Cl_2]$.[1] Treatment of **3a** with HCl gas [equation (3)] caused reaction at the tertiary alcohol at the same time as the Ir–Me bond was cleaved, to yield the phenyl chloroethyl iridium dichloro carbonyl complex **5**. This complex also shows four ring methyls in the NMR spectra, due to the presence of a chiral centre at the CPh(Me)Cl carbon, which was readily identified in the ^{13}C NMR spectrum (δ 75.3).

$$\underset{\textbf{3a}}{[\{C_5Me_4CH_2CPh(Me)OH\}IrMe(CO)Ph]} \xrightarrow{HCl} \underset{\textbf{4a}}{[\{C_5Me_4CH_2CPh(Me)OH\}IrMe(CO)Cl]} \xrightarrow{HCl} \underset{\textbf{5}}{[\{C_5Me_4CH_2CPh(Me)Cl\}Ir(CO)Cl_2]} \tag{3}$$

Under the same conditions, the diphenyl complex **4b** gave the 1,1-diphenylethene iridium dichloro carbonyl complex **6**, with loss of water [reaction (4)]. The absence of a chiral centre in **6** was immediately apparent from both the ^{13}C and the ^1H NMR spectra which showed very simple two-line spectra for the

$$\underset{\textbf{3b}}{[\{C_5Me_4CH_2CPh_2(OH)\}IrMe(CO)Ph]} \xrightarrow{HCl} \underset{\textbf{4b}}{[\{C_5Me_4CH_2CPh_2(OH)\}IrMe(CO)Cl]} \xrightarrow{HCl} \underset{\textbf{6}}{[(C_5Me_4CH{=}CPh_2)Ir(CO)Cl_2]} \tag{4}$$

Table 5 Atom coordinates for $[(C_5Me_4CH_2CPh_2OH)IrMe(CO)Ph]$ **3b**

Atom	x	y	z
Ir	1010(1)	2076(1)	2139(1)
O(1)	5159(9)	3216(10)	−944(8)
O(2)	−1274(1)	694(1)	4039(1)
O(2a)	−1662(1)	2980(1)	1172(1)
C(1)	2643(14)	2332(14)	660(11)
C(2)	3316(14)	2374(14)	1542(13)
C(3)	3048(16)	1204(15)	2561(12)
C(4)	2298(15)	448(18)	2260(14)
C(5)	2034(16)	1138(19)	1098(13)
C(6)	2711(14)	3429(14)	−585(11)
C(7)	3922(14)	3393(16)	−1488(12)
C(8)	3681(14)	2310(15)	−1774(11)
C(9)	4435(16)	1250(15)	−1357(14)
C(10)	4142(19)	259(19)	−1595(17)
C(11)	3174(22)	297(21)	−2276(17)
C(12)	2410(19)	1375(19)	−2711(14)
C(13)	2641(15)	2350(15)	−2446(13)
C(14)	4040(15)	4662(15)	−2636(12)
C(15)	3023(15)	5519(15)	−2973(12)
C(16)	3139(25)	6599(18)	−4047(12)
C(17)	4413(18)	6868(16)	−4706(14)
C(18)	5461(16)	5970(15)	−4394(13)
C(19)	5276(17)	4905(18)	−3375(13)
C(20)	4247(17)	3491(16)	1407(12)
C(21)	3725(17)	821(17)	3670(13)
C(22)	1916(17)	−957(16)	3043(13)
C(23)	1183(15)	608(16)	466(13)
C(24)	−393(1)	1227(1)	3306(1)
C(24a)	−632(1)	2631(1)	1545(1)
C(25)	989(14)	3533(14)	2599(13)
C(26)	1065(18)	4755(20)	1787(18)
C(27)	1083(18)	5763(20)	2064(18)
C(28)	1014(19)	5537(22)	3193(20)
C(29)	913(19)	4326(22)	4053(17)
C(30)	875(17)	3339(19)	3750(14)
C(31)	−389(33)	3089(32)	1094(27)
C(31a)	−239(33)	1075(34)	3624(24)

Atoms O(2), O(2a), C(24), C(24a), C(31), C(31a) have occupancies of 50%.

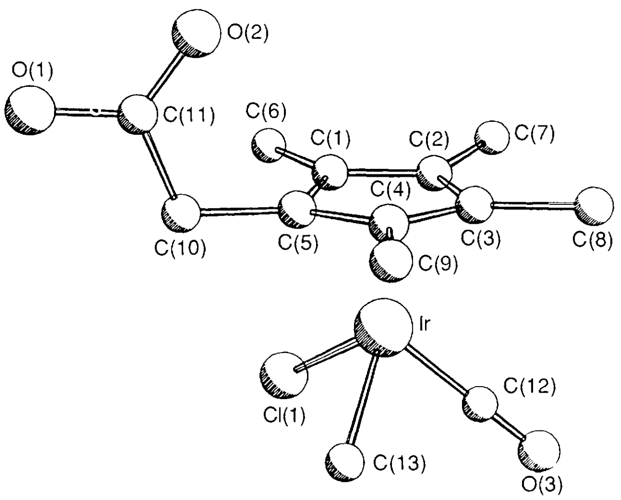


Fig. 2 A view of the structure of $[(C_5Me_4CH_2CO_2H)IrMe(CO)Cl]$ **8**, with hydrogens omitted for clarity

C_5Me_4. The ^{13}C NMR spectrum also showed the olefinic carbons -CH= at δ 115.4 and =C< at δ 151.9.

Reaction with Benzonitrile.—Organolithium reagents react with nitriles to give, after work-up, ketones.[5] A very similar reaction (5) occurred when the intermediate **2** was treated with

$$2 + \mathrm{PhCN} \xrightarrow{\mathrm{H}^+} \underset{\mathbf{7}}{[(\mathrm{C_5Me_4CH_2COPh})\mathrm{IrMe(CO)Cl}]} \quad (5)$$

benzonitrile. In this case the ketone **7** (obtained in 48% yield) was formed, cleavage of the Ir–Ph bond also having occurred. Complex **7** showed, in addition to the normal ν(Ir–CO) at 1994 cm^{-1}, a ketonic ν(CO) at 1687 cm^{-1}; again the NMR spectrum of the C_5Me_4 group showed four methyl signals, reflecting the presence of the chiral centre at Ir.

Reaction with Carbon Dioxide.—The lithio intermediate **2** also reacted very readily with carbon dioxide [reaction (6)]. The first product of the reaction, presumably $[(C_5Me_4CH_2CO_2Li)IrMe(CO)Ph]$, could be detected by IR [ν(CO_2) 1747w (br), 1714 (w–m); ν(CO) 1981vs cm^{-1}], but on work-up and treatment with HCl the product isolated (88% yield) had also lost the phenyl group and was the acetic acid derivative $[(C_5Me_4CH_2CO_2H)IrMe(CO)Cl]$ **8** [ν(CO_2) 1707w (br), ν(CO) 2016vs cm^{-1}]. This complex also showed diastereotopic C_5Me_4 in both the ^1H and the ^{13}C NMR spectra.

$$2 + \mathrm{CO_2} \xrightarrow{\mathrm{HCl}} \underset{\mathbf{8}}{[(\mathrm{C_5Me_4CH_2CO_2H})\mathrm{IrMe(CO)Cl}]} \xrightarrow{\mathrm{HCl}} \underset{\mathbf{9}}{[(\mathrm{C_5Me_4CH_2CO_2H})\mathrm{Ir(CO)Cl_2}]} \quad (6)$$

The structure of complex **8** was confirmed by a single-crystal X-ray determination (Fig. 2), which showed a tetramethylcyclopentadienyl ligand η^5 bonded to the iridium, the fifth ring substituent being an acetic acid. The metal to carbon (ring) distances are in the range 2.19–2.29 Å, the ring has a r.m.s. deviation of 0.030 Å and the metal lies 1.885 Å from the mean plane. The ring substituents deviate from this plane by up to 0.14 Å on the side away from the metal. The basal sites on the metal are occupied by one chlorine, one methyl and one carbonyl; the chlorine and the CO ligands are mutually disordered with one configuration (as shown) preferred (62:38%). The methyl group is ordered. The bond angles between the basal ligands are close to 90°. Molecules of complex **8** are linked across a crystallographic inversion centre (at 0.5, 0, 0.5) by pairs of strong hydrogen bonds between the carboxylic acid residues (O ··· O 2.670 Å). This is characteristic of the solid-state structures of carboxylic acids.[6] No other significant intermolecular contacts were found.

The tetramethylcyclopentadienylacetic acid complex **8** showed a pK_a of 4.65 in ethanol–water (1:1), which makes it a significantly stronger acid than uncomplexed benzoic (pK_a 5.54) or phenylacetic acid (pK_a 5.59) in the same solvent system. It is however close to the value reported (pK_a 4.52) for the chromium tricarbonyl complex of benzoic acid.[7] This suggests that Ir^{III} acts in a comparable electron-withdrawing sense to Cr^0(CO)$_3$ for this system.

Extended treatment of complex **8** with HCl cleaved the iridium–methyl bond and yielded the carbonyl dichloride complex **9**.

Since complex **8** was acid-sensitive, it was esterified under basic conditions, by reaction with methanol, in the presence of 4-dimethylaminopyridine and dicyclohexylcarbodiimide,[8] to yield **10a** [equation (7)]. Reaction of the same complex with the

Table 6 Selected bond lengths (Å) and angles (°) for $[(C_5Me_4CH_2CO_2H)IrMe(CO)Cl]$ **8**

Ir–Cl(1)	2.358(11)	Ir–Cl(1a)	2.357(14)
Ir–C(1)	2.291(15)	Ir–C(2)	2.277(15)
Ir–C(3)	2.225(17)	Ir–C(4)	2.260(20)
Ir–C(5)	2.191(17)	Ir–C(13)	2.119(18)
O(1)–C(11)	1.299(21)	O(2)–C(11)	1.249(19)
C(12)–Ir–Cl(1)	91.0(3)	Cl(1a)–Ir–C(13)	87.9(7)
C(12a)–Ir–Cl(1a)	94.2(4)	C(5)–C(10)–C(11)	113.8(13)
C(12)–Ir–C(13)	82.6(6)	O(1)–C(11)–O(2)	121.2(16)
C(12a)–Ir–C(13)	87.8(5)	O(1)–C(11)–C(10)	116.6(14)
Cl(1)–Ir–C(13)	88.4(6)	O(2)–C(11)–C(10)	122.1(16)

Table 7 Atom coordinates for $[(C_5Me_4CH_2CO_2H)IrMe(CO)Cl]$ **8**

Atom	*x*	*y*	*z*
Ir	71(1)	3133(1)	2229(1)
Cl(1)	−1143(13)	5236(15)	3340(6)
Cl(1a)	−1086(18)	3956(21)	879(8)
O(1)	2668(16)	240(19)	5218(8)
O(2)	4484(16)	786(20)	4030(8)
O(3)	−1844(1)	4094(1)	580(1)
O(3a)	−1552(1)	5803(1)	3643(1)
C(1)	2951(20)	4003(21)	3089(11)
C(2)	3258(20)	4083(23)	2109(12)
C(3)	2517(21)	2265(23)	1535(11)
C(4)	1788(22)	1010(23)	2148(11)
C(5)	1917(20)	2120(21)	3098(10)
C(6)	3524(28)	5585(30)	3936(16)
C(7)	4412(25)	5765(28)	1744(17)
C(8)	2749(28)	1646(31)	455(13)
C(9)	965(32)	−1059(25)	1874(18)
C(10)	1448(21)	1446(26)	4026(12)
C(11)	2963(20)	783(22)	4421(10)
C(12)	−1099(1)	3715(1)	1220(1)
C(12a)	−914(1)	4767(1)	3093(1)
C(13)	−2567(27)	1166(27)	2164(13)

Atoms Cl(1), O(3), C(12) have occupancies of 62%, Cl(1a), O(3a), C(12a) of 38%.

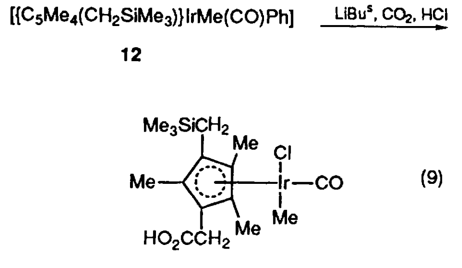
$$\underset{\mathbf{8}}{[(C_5Me_4CH_2CO_2H)IrMe(CO)Cl]} \xrightarrow[\text{base}]{+ROH,\ -H_2O} \underset{\mathbf{10}}{[(C_5Me_4CH_2CO_2R)IrMe(CO)Cl]} \quad (7)$$

optically active alcohol 1*R*,2*S*,5*R*-menthol gave the optically active ester **10b**, optical rotation α (589 nm, 25 °C, 10 mg in 1 cm^3 $CHCl_3$) = −32.3°. The molecule has two chiral centres, one at iridium (unresolved), the other at the menthyl group, which is optically active; thus complex patterns were observed in both the ^1H and the ^{13}C NMR spectra of the C_5Me_4 group.

Since complex **9** was not acid-sensitive it could be esterified under conventional acidic conditions. The ethyl ester **11** was made, in 91% yield, by reaction (8) of **9** with ethanol in the presence of HCl.

$$\underset{\mathbf{9}}{[(C_5Me_4CH_2CO_2H)Ir(CO)Cl_2]} \xrightarrow{EtOH/H^+} \underset{\mathbf{11}}{[(C_5Me_4CH_2CO_2Et)Ir(CO)Cl_2]} \quad (8)$$

In Part 1,[1] it was shown that the trimethylsilylmethyl complex **12** itself underwent metallation with *sec*-butyllithium, which on reaction with chlorotrimethylsilane gave $[\{C_5Me_3(CH_2SiMe_3)_2\}IrMe(CO)Ph]$. The two trimethylsilylmethyl groups were shown to be 1,3 on the C_5Me_3 ring by an X-ray determination,[1] indicating that metallation of **12** occurred at a methyl separated by one carbon from the first. We have used the same reaction (9) on **12** to introduce a carboxylic acid function,



(9)

by treating it with *sec*-butyllithium followed by carbon dioxide. Complex **13**, which presumably also has the ring substituents 1,3, was obtained in 79% yield after work-up. The spectroscopic data agree with the proposed formulation.

Conclusion

The ring-metallated species **2** derived from **1** can react with various carbonyl compounds (ketones and CO_2) as well as with organic and organoelement halides. In addition we have found that benzonitrile will react with **2**, to give a ketone, after work-up. This shows that a very rich area of organometallic chemistry is ready to be exploited. The substitution reactions discussed here and in Part 1 allow a wide variety of pendant groups to be attached, and in later papers we will be discussing how these control reactions at the metal centre.

Both $[(C_5Me_5)IrMe(CO)Ph]$[1,3] and $[(C_5Me_5)IrMe_4]$[1] are quite readily metallated. We have also recently shown that the cations $[(C_5Me_5)M(C_5H_5)]^+$ (M = Rh[2] or Ir[9]) can be deprotonated by strong bases to give species which are also attacked by nucleophilic reagents such as alkyl halides. We are now expanding the range of complexes and bases which can undergo such reactions in order to elicit the reason for the preferences exhibited.

Experimental

All operations were carried out under dry nitrogen using standard Schlenk techniques. Solvents were purified and then distilled under nitrogen prior to use. Microanalyses, performed by the University of Sheffield microanalysis service, yields and IR data (PE-1600 FT-IR spectrometer) are collected in Table 1, ^1H NMR (Bruker AM-250) in Table 2, and ^{13}C NMR (Bruker AM-250) in Table 3. Typical procedures are detailed below; the amount of active *sec*-butyllithium in the solution was determined by titration.[10]

$[\{C_5Me_4CH_2CPh(Me)OH\}IrMe(CO)Ph]$ **3a**.—Dry tetrahydrofuran (5 cm^3) was injected into a Schlenk tube (capacity 100 cm^3) containing $[(C_5Me_5)IrMe(CO)Ph]$[4] **1** (0.2 g, 0.446 mmol), a magnetic stirrer, and capped with a Suba-seal, and the resultant colourless solution was cooled (−78 °C). *sec*-Butyllithium (360 μl, Aldrich; 1.2 mol dm^{-3} in cyclohexane; Li:Ir ratio 1.5:1) was then injected. The colour changed to yellow. The solution was stirred (−78 °C, 1 h), after which acetophenone (63 μl, 0.54 mmol) was added. The solution was stirred (1 h, −78 °C), allowed to warm (20 °C) and stirred for 1 h after which it was again cooled (−78 °C) and a saturated aqueous solution of ammonium chloride (0.5 cm^3) was added. After warming (to 20 °C), the solvent was removed *in vacuo*, and the residual oily solid was extracted with pentane (4 × 10 cm^3) and then chromatographed on neutral alumina (3% deactivated), first with pentane (which gave 0.02 g of starting material), then with pentane–diethyl ether (3:2) to yield $[\{C_5Me_4CH_2CPh(Me)OH\}IrMe(CO)Ph]$ **3a** (0.200 g, 79%) after crystallisation from pentane at −20 °C.

[{$C_5Me_4CH_2CPh(Me)OH$}$IrMe(CO)Cl$] **4a**.—A stream of dry hydrogen chloride gas was bubbled [1 atm (*ca.* 10^5 Pa), 20 °C, 2 min] through a stirred solution of [{$C_5Me_4CH_2CPh(Me)OH$}$IrMe(CO)Ph$] **3a** (0.115 g, 0.202 mmol) in dichloromethane (20 cm^3). The colour turned yellow. Dry nitrogen was then bubbled through to remove excess of HCl gas; the solution was dried ($MgSO_4$), and the solvent removed *in vacuo* to give a yellow solid which was chromatographed on neutral alumina (3% deactivated). Elution with diethyl ether gave a yellow solution, which yielded [{$C_5Me_4CH_2CPh(Me)OH$}$IrMe(CO)Cl$] **4a** (0.078 g, 73%) after recrystallisation from dichloromethane–hexane at −20 °C.

[{$C_5Me_4CH_2CPh(Me)Cl$}$Ir(CO)Cl_2$] **5**.—A stream of dry hydrogen chloride gas was gently bubbled (4 min) through a stirred solution of [{$C_5Me_4CH_2CPh(Me)OH$}$IrMe(CO)Ph$] **3a** (0.102 g, 0.211 mmol) in dichloromethane (20 cm^3). The colour turned yellow. The solution was set aside (24 h), then again saturated with HCl gas and set aside (4 d). [During this time the solution was monitored by IR spectroscopy to determine the extent of reaction by measuring the peak heights of **4a**, ν(CO) 2011 cm^{-1}, and **5**, ν(CO) 2061 cm^{-1}.] Dry nitrogen was then bubbled through to remove excess of HCl gas; the solution was dried ($MgSO_4$), filtered, and the solvent removed *in vacuo* to give an orange-yellow solid, which was washed with hexane (3 × 10 cm^3) and crystallised from dichloromethane–hexane to give [{$C_5Me_4CH_2CPh(Me)Cl$}$Ir(CO)Cl_2$] **5** (0.082 g, 67%). Analogous reaction of **3b** (0.10 g) gave **6**, [($C_5Me_4CH{=}CPh_2$)$Ir(CO)Cl_2$] (0.082 g, 88%).

[($C_5Me_4CH_2COPh$)$IrMe(CO)Cl$] **7**.—The lithio complex **2** prepared as above for **3a** from **1** (0.15 g, 0.335 mmol) was treated at −78 °C with benzonitrile (42 μl; Li/N ratio 1:1). Conventional work-up, followed by chromatography (neutral alumina, 3% deactivated) in pentane–diethyl ether (2:1) gave a colourless solution which yielded crystals of **7** from pentane at −20 °C. Yield 0.098 g (48%).

[($C_5Me_4CH_2CO_2H$)$IrMe(CO)Cl$] **8**.—The lithio complex **2** prepared as above for **3a** from **1** (0.500 g, 1.12 mmol) was treated with solid CO_2 (*ca.* 1 g) under a stream of nitrogen; the yellow colour faded immediately. The solution was stirred (30 min, −78 °C), then a saturated aqueous solution of ammonium chloride (0.5 cm^3) was added and the solution allowed to warm (to +20 °C); carbon dioxide was evolved. The solvent was removed *in vacuo*, and the residual white solid redissolved in dichloromethane (30 cm^3). On bubbling dry hydrogen chloride gas slowly through that solution (2 min) the colour turned yellow. This was accompanied by a change in the IR spectrum from that of the presumed first product, [($C_5Me_4CH_2CO_2Li$)$IrMe(CO)(Ph)$] [ν(CO_2) 1747w (br), 1714w–m; ν(CO) 1981vs cm^{-1}] to that of the final product, [($C_5Me_4CH_2CO_2H$)$IrMe(CO)Cl$] [ν(CO_2) 1707vs, ν(CO) 2016vs cm^{-1}]. The solution was dried ($MgSO_4$), filtered through Celite, and concentrated *in vacuo* (to 2 cm^3); on addition of hexane (50 cm^3) a yellow precipitate formed which was filtered off, washed (hexane, 4 × 10 cm^3) and air-dried to give [($C_5Me_4CH_2CO_2H$)$IrMe(CO)Cl$], yield 0.458 g (92%).

[($C_5Me_4CH_2CO_2H$)$Ir(CO)Cl_2$] **9**.—A stirred solution of complex **8** (0.282 g, 0.627 mmol) in dichloromethane (50 cm^3) was treated with dry hydrogen chloride gas as for **5**, above. After work-up and crystallisation from dichloromethane–hexane, [($C_5Me_4CH_2CO_2H$)$Ir(CO)Cl_2$] **9** (0.276 g, 94%) was obtained.

[($C_5Me_4CH_2CO_2Me$)$IrMe(CO)Cl$] **10a**.—A solution of dicyclohexylcarbodiimide (0.060 g, 0.278 mmol) and 4-dimethylaminopyridine (0.003 g, 0.022 mmol) in dry dichloromethane (1.5 cm^3, distilled from CaH_2) was added by syringe to a stirred solution of [($C_5Me_4CH_2CO_2H$)$IrMe(CO)Cl$] (0.1 g, 0.222 mmol) and methanol (10 μl) in dry dichloromethane (5 cm^3). After stirring (5 h, 20 °C) the solvent was removed *in vacuo*, and the yellow residue extracted with hexane (3 × 10 cm^3). This extract was chromatographed on an alumina column (8 × 2.5 cm), using hexane–diethyl ether (1:1) to elute a yellow band which gave yellow crystals of [($C_5Me_4CH_2CO_2Me$)$IrMe(CO)Cl$], yield 0.056 g (54%).

[($C_5Me_4CH_2CO_2C_{10}H_{19}OH$)$IrMe(CO)Cl$] **10b**.—An analogous reaction of [($C_5Me_4CH_2CO_2H$)$IrMe(CO)Cl$] (0.200 g, 0.444 mmol) and 1*R*,2*S*,5*R*-menthol (0.070 g, acid:menthol ratio 1:1) yielded gave yellow [($C_5Me_4CH_2CO_2C_{10}H_{19}OH$)$IrMe(CO)Cl$] **10b**, recrystallised from hexane at −20 °C [0.188 g, 57%; optical rotation α (589 nm, 25 °C, 10 mg in 1 cm^3 $CHCl_3$) = −32.3°].

[($C_5Me_4CH_2CO_2Et$)$Ir(CO)Cl_2$] **11**.—A stream of dry hydrogen chloride gas was gently bubbled (4 min) through a stirred solution of [($C_5Me_4CH_2CO_2H$)$Ir(CO)Cl_2$] **9** (0.075 g, 0.159 mmol) and ethanol (2 cm^3) in dichloromethane (5 cm^3). The solution was stirred (3 h at 25 °C) while being monitored by IR spectroscopy. When the reaction was complete, HCl gas and the solvent were removed *in vacuo*, and the residue crystallised from dichloromethane–hexane to give [($C_5Me_4CH_2CO_2Et$)$Ir(CO)Cl_2$] **11**, total yield 0.070 g (91%).

[{$C_5Me_3(CH_2CO_2H)(CH_2SiMe_3)$}$IrMe(CO)Cl$] **13**.—A solution of the lithio complex prepared as above for **3a** from **12** [{$C_5Me_4(CH_2SiMe_3)$}$IrMe(CO)Ph$] (0.405 g, 0.78 mmol), at −78 °C was treated with solid CO_2 (*ca.* 1.5 g). The yellow colour faded immediately; the solution was stirred (30 min, −78 °C), and then worked up as for complex **8** above to give [{$C_5Me_3(CH_2CO_2H)(CH_2SiMe_3)$}$IrMe(CO)Cl$] **13**, yield 0.322 g (79%).

Crystal Structure Determination of [(η^5-$C_5Me_4CH_2CPh_2OH$)$IrMe(CO)Ph$] **3b**.—*Crystal data.* $C_{31}H_{33}IrO_2$, M = 629.80, crystallised from pentane as yellow prisms, crystal dimensions 0.70 × 0.40 × 0.20 mm, triclinic, space group $P\bar{1}$ (C_i^1, no. 2), a = 9.776(23), b = 12.014(27), c = 13.129(38) Å, α = 63.41(20), β = 83.22(22), γ = 89.02(19)°, U = 1368(6) Å^3, D_c = 1.529 g cm^{-3}, Z = 2, Mo-Kα radiation (λ = 0.710 69 Å), μ(Mo-Kα) = 48.83 cm^{-1}, $F(000)$ = 623.85.

Three-dimensional, room-temperature X-ray data were collected in the range 3.5 < 2θ < 50° on a Nicolet R3 four-circle diffractometer by the ω-scan method. The 2813 independent reflections (of 4793 measured) for which $|F|/\sigma(|F|) > 3.0$ were corrected for Lorentz and polarisation effects, and for absorption by analysis of seven azimuthal scans (minimum and maximum transmission coefficients 0.058 and 0.106). The structure was solved by Patterson and Fourier techniques and refined by blocked-cascade least-squares methods. The methyl and carbonyl ligands were found to be equally disordered between two basal sites and were refined with geometric contraints (linear Ir–C–O; Ir–C 1.85, C–O 1.16 Å); the two Ir–Me distances were constrained to be equal. Hydrogen atoms were included in calculated positions, with isotropic thermal parameters related to those of the supporting atom, and refined in riding mode: the hydrogen related to O(1) was not located. Refinement converged at a final R 0.0748 (R' 0.0659, 294 parameters; mean and maximum final Δ/σ 0.039 and 0.163 respectively), with allowance for the thermal anisotropy of all non-hydrogen atoms, with the exception of those of the disordered carbonyl and methyl groups which were given a common isotropic thermal parameter. A final difference electron-density synthesis showed minimum and maximum values of −1.30 and +1.01 e Å^{-3}. Complex scattering factors were taken from ref. 11 and from the program package SHELXTL[12] as implemented on a Data General Nova 3 computer. A weighting scheme $w^{-1} = [\sigma^2(F) + 0.000\,78F^2]$ was used in the latter stages of refinement. Important bond lengths and angles are collected in Table 4 while atom coordinates are in Table 5.

Crystal Structure Determination of [(η^5-$C_5Me_4CH_2CO_2H$)-Ir(Me)(CO)Cl] **8**.—*Crystal data.* $C_{13}H_{18}ClIrO_3$, M = 449.94, crystallised from dichloromethane–pentane as yellow blocks, crystal dimensions 0.50 × 0.225 × 0.225 mm, triclinic, space group $P\bar{1}$ ($C_i^{\,1}$, no. 2), a = 7.274(9), b = 7.634(14), c = 14.34(4) Å, α = 102.01(19), β = 90.97(18), γ = 103.96(13)°, U = 754.2(28) Å^3, D_c = 1.981 g cm^{-3}, Z = 2, Mo-Kα radiation (λ = 0.710 69 Å), μ(Mo-Kα) = 89.95 cm^{-1}, F(000) = 427.88.

Three-dimensional, room-temperature X-ray data were collected as for complex **3b**. The 2170 independent reflections (of 2658 measured) for which $|F|/\sigma(|F|) > 3.0$ were corrected for Lorentz and polarisation effects, and for absorption by analysis of four azimuthal scans (minimum and maximum transmission coefficients 0.009 and 0.028). The structure was solved and refined as for **3b**. The chlorine and the carbonyl ligands were found to be unequally disordered (0.62:0.38) between two basal sites and were refined with geometric contraints (linear Ir–C–O; Ir–C 1.85, C–O 1.18 Å); the two Ir–Cl distances were constrained to be equal. Surprisingly, the disorder did not involve the basal methyl group, as was the case in **3b**. Hydrogen atoms were treated as for **3b**. Refinement converged at a final R 0.0587 (R' 0.0595, 166 parameters; mean and maximum final Δ/σ 0.002 and 0.031 respectively), with allowance for the thermal anisotropy of all non-hydrogen atoms, with the exception of those of the disordered carbonyl groups which were given a common isotropic thermal parameter. A final difference electron-density synthesis showed minimum and maximum values of −2.25 and +1.46 e Å^{-3}. The sources of the complex scattering factors were as for **3b**. A weighting scheme $w^{-1} = [\sigma^2(F) + 0.002\,00F^2]$ was used in the latter stages of refinement. Important bond lengths and angles are collected in Table, 6 atom coordinates in Table 7.

Additional material for both structures available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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