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Ring-methyl activation in pentamethylcyclopentadienyliridium complexes; synthesis of $[(C_5Me_4CH_2E)IrL_n]$ ($E = SiMe_3$, $PhCH_2$, $CH_2{=}CHCH_2$, PPh_2, and $Pt(PEt_3)_2Cl$), and synthesis and X-ray structure of $[(1,3\text{-}C_5Me_3(CH_2SiMe_3)_2)Ir(CO)Me(Cl)]$ *

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Abstract

The pentamethylcyclopentadienyliridium complex $[C_5Me_5Ir(Me)CO(Ph)]$ (**1**) is metallated by sec-BuLi at a ring methyl. The lithio-complex intermediate, presumably $Li[(C_5Me_4CH_2)Ir(Me)CO(Ph)]$ (**2**) reacts with various halides (E–X) to give the appropriately substituted $[(C_5Me_4CH_2E)Ir(Me)CO(Ph)]$ (**3**) ($E = SiMe_3$, **a**; $PhCH_2$, **b**; $CH_2{=}CHCH_2$, **c**; PPh_2, **d**; and $Pt(PEt_3)_2Cl$, **e**). The Ir–Ph bond in **3a–c** is cleaved by HCl to give $[(C_5Me_4CH_2E)Ir(Me)CO(Cl)]$ (**4a–c**), which are in turn converted into $[(C_5Me_4CH_2E)IrCO(Cl)_2]$ (**5a–c**) with more HCl, and then into $[\{(C_5Me_4CH_2E)Ir(Cl)_2\}_2]$ (**6a–b**) on heating. The butenyl complex, $[(C_5Me_4CH_2CH_2CH{=}CH_2)IrCl_2]$ (**6c**) is monomeric with an internally coordinated double bond. Two equivalents of **2** react with $SiMe_2Cl_2$ to give $[Me_2Si\{CH_2C_5Me_4Ir(Me)\text{-}CO(Ph)\}_2]$ (**7**). The di-iridium complex $[(C_5Me_4CH_2SiMe_3)IrCl_2(PPh_2CH_2C_5Me_4)Ir(Me)CO(Ph)]$ (**8**) is formed on reaction of **3d** with **6a**. The complex **3a** could be remetallated by sec-BuLi and converted into the bistrimethylsilylmethylene complex $[(C_5Me_3(CH_2SiMe_3)_2)Ir(Me)CO(Ph)]$ (**9**). The 1,3-disposition of the Me_3SiCH_2 groups on the ring was shown by an X-ray structure determination of $[(C_5Me_3(CH_2E)_2)\text{-}Ir(Me)CO(Cl)]$ (**10**). Complex $[C_5Me_5IrMe_4]$ (**11**) was also metallated by sec-BuLi and could be converted into $[(C_5Me_4CH_2E)Ir(Me)_4]$ (**12**) ($E = SiMe_3$, **a**; Et, **f**).

Introduction

The pentamethylcyclopentadienyliridium complexes have attracted substantial attention since their discovery in 1969 [1]. Their very useful properties, arising from the combination of an inert and stable ring-to-metal bond on one side of the metal and labile ligands on the other, have 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 are prepared from the appropriately substituted cyclopentadienes and iridium trichlo-

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* Dedicated, with all good wishes, to Professor Peter L. Pauson on the occasion of his retirement.

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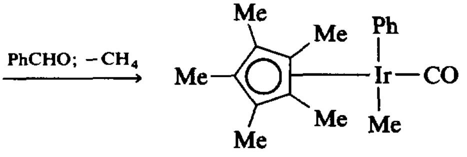
ride. These are not always easy of access, and the method of preparation severely limits the functional groups which may be introduced.

Some time ago we found 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]. This suggested some stability for η^4-tetramethylfulvene species eg, $[C_5Me_4CH_2ML_n]^-$, and indicated that it should be possible to use the reaction synthetically to functionalise a methyl. After some unsuccessful trials, we have now succeeded in doing this and we here 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 (E). This paper is concerned with the basic reaction with a variety of organic and other halides, and also with double substitution. In a further paper we will describe the reactions to give oxy-species. A part of the work has already been communicated [5]. Gloagen and Astruc have recently reported the polyalkylation of $[Co(C_5Me_5)(C_5H_5)]^+$ by reaction with KO^tBu and alkyl halides [6]; that appears to be the only other example of ring-methyl functionalisation in a C_5Me_5 ring. By contrast, methyls on η^6-arenes are quite easily alkylated [7].

Results and discussion

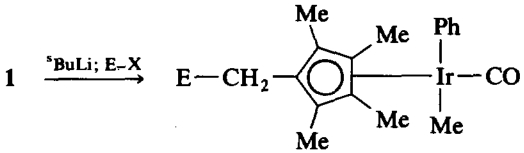
The metallation of $[C_5Me_5Ir(Me)CO(Ph)]$ (1)

$$[\{(C_5Me_5)Ir\}_2Cl_4] \xrightarrow{Me_2SO;\ Al_2Me_6} [(C_5Me_5)Ir(Me)_2(Me_2SO)]$$



(1)

The pentamethylcyclopentadienyliridium(III) complex $[C_5Me_5Ir(Me)CO(Ph)]$ **1**, obtained by the route shown above [8], is metallated by sec-BuLi at a ring methyl:



(**3**: E = $SiMe_3$, **a**; $PhCH_2$, **b**; CH_2=$CHCH_2$, **c**; PPh_2, **d**; and $Pt(PEt_3)_2Cl$, **e**)

Metallation occurs readily in THF at −78°C and only a small excess of the butyllithium needs to be used to ensure complete conversion. The product of this metallation has not yet been defined but is probably the lithio-complex $Li[(C_5Me_4CH_2)Ir(Me)CO(Ph)]$ (**2**). This reacts with various halides (E–X, Me_3SiCl, $PhCH_2Cl$, CH_2=$CHCH_2Br$, or PPh_2Cl) to give the appropriately substituted $[(C_5Me_4CH_2E)Ir(Me)CO(Ph)]$ (**3**: E = $SiMe_3$, **a**; $PhCH_2$, **b**; CH_2=$CHCH_2$, **c**; PPh_2, **d**) in good to excellent yield. These complexes all show the expected spectroscopic properties; thus, for example, $\nu(CO)$ is in the region 1992–1995 cm^{-1} (Table 1), very similar to that for **1** at 1994 cm^{-1}. The iridium in **3** is a chiral centre and the

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Table 1

Microanalytical, IR and yield data

Complex	E	ν(CO) [a] (cm^{-1})	Microanalysis [b]			Yield (%)
			%C	%H	%Cl	
3a	$SiMe_3$	1992	48.6	6.1	–	89
			(48.5)	(6.0)	–	
3b	CH_2Ph	1995	55.9	5.4	–	70
			(55.8)	(5.4)	–	
3c	$CH_2CH{=}CH_2$	1995	51.6	5.5	–	91
			(51.7)	(5.6)	–	
3d	PPh_2	1994	56.6	5.1	–	56
			(57.0)	(5.1)	–	
3e	*trans*-$Pt(PEt_3)_2Cl$	1989	39.4	5.6	3.8	76
			(39.5)	(5.7)	(3.9)	
	cis-$Pt(PEt_3)_2Cl$	1963 [c]	39.4	5.6	3.9	–
			(39.5)	(5.7)	(3.9)	
4a	$SiMe_3$	2007 [c]	37.8	5.6	7.6	90
			(37.7)	(5.5)	(7.4)	
4b	CH_2Ph	2011 [c]	46.2	4.9	7.3	85
			(46.0)	(4.9)	(7.2)	
4c	$CH_2CH{=}CH_2$	2011 [c]	40.8	5.0	7.8	68
			(40.4)	(5.0)	(8.0)	
5a	$SiMe_3$	2055 [c]	33.8	4.6	14.4	95
			(33.7)	(4.7)	(14.2)	
5b	CH_2Ph	2059 [c]	41.7	3.9	13.6	89
			(41.9)	(4.1)	(13.7)	
5c	$CH_2CH{=}CH_2$	2059 [c]	36.1	4.1	15.0	85
			(36.1)	(4.1)	(15.2)	
6a	$SiMe_3$	–	33.3	5.0	14.9	86
			(33.2)	(4.9)	(15.1)	
6b	$CH_2Ph\cdot\frac{1}{3}CH_2Cl_2$	–	41.1	4.4	16.2	77
			(41.0)	(4.3)	(16.4)	
6d [d]	$CH_2CH{=}CH_2$	–	35.7	4.2	15.9	95
			(35.6)	(4.4)	(16.2)	
7		1994	48.5	5.5	–	71
			(48.0)	(5.3)	–	
8		1994 [c]	47.1	4.9	6.5	75
			(46.9)	(5.0)	(6.4)	
10		2012	39.2	6.0	6.4	76
			(39.4)	(5.9)	(6.5)	
12a		–	44.5	7.8	–	71
			(44.4)	(7.7)	–	
12f		–	46.2	7.3	–	67
			(46.2)	(7.5)	–	

[a] In pentane. [b] Found and calculated (in parentheses). [c] In CH_2Cl_2. [d] Osmometric molecular weight: found (in $CHCl_3$), 479; calculated for monomeric $[\{C_5Me_4(CH_2)_2CH{=}CH_2\}IrCl_2]$, 438.

Table 2

^{1}H NMR spectra ($CDCl_3$ solution; δ ppm from TMS; all singlets unless otherwise indicated)

Complex	E	C_5Me_4	Me–Ir	Ph–Ir	CH_2–R	R
3a	$SiMe_3$	1.72 (3H), 1.74 (3H), 1.76 (6H)	0.62	6.95m 7.14m	1.54	$SiMe_3$, 0.00
3b	CH_2Ph	1.61 (3H), 1.64 (3H), 1.70 (3H), 1.73 (3H)	0.63	6.94m 7.12m	2.43m	CH_2, 2.68m; Ph, 7.12 (2H), 7.25m (3H)
3c	$CH_2CH{=}CH_2$	1.70 (3H), 1.74 (6H), 1.80 (3H)	0.64	6.95m 7.15m	2.23m	CH_2, 2.14m; H^1, 5.79m ($J(H^2)$ 17, $J(H^3)$ 10, $J(CH_2)$ 6.5 Hz) [a]; H^2, 5.01m ($J(H^3)$ 1.6, $J(CH_2)$ 1.5 Hz) [a]; H^3, 4.98m ($J(CH_2)$ 1.0 Hz) [a]
3d	PPh_2 [b]	1.37 (3H), 1.39 (6H), 1.71 (6H)	0.62	6.94m 7.11m	2.82m	Ph, 7.32m
3e	*t*-$Pt(PEt_3)_2Cl$ [c]	1.69 (3H), 1.81 (3H), 1.93 (3H), 2.12 (3H)	0.59	6.94m 7.12m	2.05tt [d]	CH_3, 1.14 [m, 8 Hz]; CH_2, 1.68m
3e	*c*-$Pt(PEt_3)_2Cl$ [e]	1.65(3H), 1.87 (3H), 1.90 (3H), 1.95 (3H)	0.54	6.89m 7.20m	1.47m [f] 1.43m [f]	CH_3, 1.01 [t, 8 Hz], 1.07m; CH_2, 1.86m, 1.63m
4a	$SiMe_3$	1.81 (3H), 1.82 (3H), 1.86 (3H), 1.90 (3H)	1.12	–	1.65m	$SiMe_3$, 0.06
4b	CH_2Ph	1.65 (3H), 1.72 (3H), 1.80 (3H), 1.86 (3H)	1.04	–	2.48m	CH_2Ph, 2.75 [t, 8 Hz]; Ph, 7.08m (2H), 7.24m (3H)
4c	$CH_2CH{=}CH_2$	1.82 (3H), 1.85 (3H), 1.87 (3H), 1.91 (3H)	1.16	–	2.29m	CH_2, 2.20m; H^1, 5.79m ($J(H^2)$ 17, $J(H^3)$ 10, $J(CH_2)$ 6.5 Hz) [a]; H^2, 5.05m ($J(H^3)$ 1.5, $J(CH_2)$ 1.5 Hz) [a]; H^3, 5.02m [a]
5a	$SiMe_3$	1.86 (6H), 1.93 (6H)	–	–	1.78	$SiMe_3$, 0.11 (9H)
5b	CH_2Ph	1.69 (6H), 1.87 (6H)	–	–	2.58t	CH_2Ph, 2.84t (2H, 7 Hz); Ph, 7.09m (2H), 7.28m (3H)

5c	$CH_2CH{=}CH_2$	1.91 (6H), 1.95 (6H)	–	–	2.40m	CH_2, 2.29m; H^1, 5.79m; H, 5.11m; H^3, 5.05m[a]
6a	$SiMe_3$	1.56 (6H), 1.58 (6H)	–	–	1.51	Me_3Si, 0.01 (9H)
6b	CH_2Ph	1.35 (6H), 1.54 (6H)	–	–	2.45td (7.5; 0.7)	CH_2, 2.74 (t, 7.5 Hz); Ph, 7.02m (2H), 7.20m (3H)
6c	$CH_2CH{=}CH_2$ [a]	1.79 (6H), 1.90 (6H)	–	–	2.52t (7.5)	CH_2, 3.11 (td, 15 and 5 Hz); H^1, 5.49 (m, $J(H^2)$ 13, $J(H^3)$ 8, $J(CH_2)$ 5 Hz); H^2, 4.32 (dt, $J(H^1)$ 13, $J(H^3)$ 1 Hz); H^3, 4.58 (d, 8 Hz) [a]
7		1.64 (3H), 1.68 (3H), 1.78 (3H), 1.82 (3H)	0.60	6.95m 7.11m	1.43	$SiMe_2$, −0.04
8 [h]		0.87 (3H), 0.98 (3H), 1.21 (3H), 1.22 (3H), 1.39 (3H), 1.40 (3H), 1.41 (3H), 1.50 (3H)	0.58	6.90m 7.05m	1.19m 3.90d [i]	$SiMe_3$, −0.05; PPh_2, 7.35m, 7.75m
9		1.73 (6H), 1.76 (3H)	0.61	6.96m 7.15m	1.58	$SiMe_3$, 0.02
10		1.80 (3H), 1.82 (3H), 1.85 (3H)	1.00	–	1.68m	$SiMe_3$, 0.06
12a [j]		1.10 (6H), 1.11 (6H)	0.98	–	0.94	$SiMe_3$, −0.13
12f [j]		1.04 (6H), 1.13 (6H)	1.01	–	1.50m	CH_2, 1.22m; CH_3, 0.74 (t, $J = 7$ Hz)

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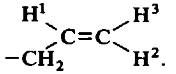
[a] Assignment of allylic resonances:



[b] $^{31}P\{^1H\}$ NMR ($CDCl_3$ solution) −16.5 ppm. [c] $^{31}P\{^1H\}$ NMR ($CDCl_3$ solution) +11.9 ppm, [J(Pt–P) 2879 Hz]. [d] [^2J(Pt–H) 110 Hz], [^3J(P–H) 6 Hz]. [e] $^{31}P\{^1H\}$ NMR ($CDCl_3$ solution) $\delta(P_a)$ +13.2 ppm [$^1J(Pt\text{–}P_a)$ 4222 Hz, $^2J(P_a\text{–}P_b)$ 16 Hz]; $\delta(P_b)$ +7.8 ppm [($J(Pt\text{–}P_b)$ 1746 Hz]. [f] $^3J(P_a\text{–}H)$ 9 Hz, $^3J(P_b\text{–}H)$ 3 Hz. [g] Spectrum at +24°C; at −50°C in $CDCl_3$ resonances were observed at δ 1.69, 1.74, 1.94, 2.04 (4×Me), 5.46 (m, H^1), 4.36 (d, 13 Hz, H^2), 5.48 (d, 8 Hz, H^3), 3.26 and 2.96 (2×m, CH_2), 2.50 (m, CH_2); see text. [h] $^{31}P\{^1H\}$ NMR ($CDCl_3$ solution) −1.92 ppm. [i] d, J(P–H) 8 Hz. [j] in C_6D_6.

Table 3

^{13}C NMR spectra ($CDCl_3$ solution; $J(P-C)$ in parentheses in Hz)

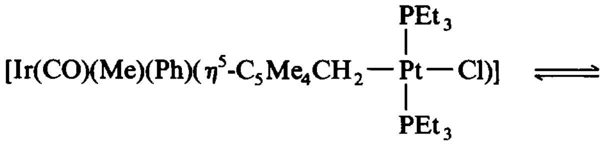
Complex	E	C_5Me_4	Me–Ir	Ph–Ir (C^4, $C^{3,5}$, C^1, $C^{2,6}$)	CO	CH_2R	R
3a	$SiMe_3$	8.8, 8.9, 9.5, 9.6 94.4, 94.6, 98.1	−21.3	122.6, 127.8, 131.6, 139.7	173.1	13.6	−0.6 ($SiMe_3$)
3b	CH_2Ph	8.5, 8.5, 8.6, 8.6 97.9, 98.0, 99.2, 99.8, 99.8	−22.4	122.7, 127.9, 130.4, 139.8	172.6	26.4	36.7 (CH_2); Ph, 126.2 C^4, 128.4, 128.6 C^{2-3}, 141.0 C^1
3c	$CH_2CH{=}CH_2$	8.5, 8.9 97.8, 97.9, 98.9, 99.5, 100.4	−22.3	122.7, 127.9, 130.4, 139.8	172.7	23.7	34.8 (CH_2), 115.4 (=CH_2) 137.5 (CH=)
3d	PPh_2	8.6, 8.7, 8.8, 8.8, 97.1, 97.4, 98.3, 98.7, 99.2(19)	−21.7	122.8, 128.0, 130.7, 139.6	172.6	24.7 (17)	P–Ph_2, C^1 137.7 (16), $C^{3,5}$ 128.5(7), C^4 129.0, $C^{2,6}$ 133.1 (19)
3e	*t*-$Pt(PEt_3)_2Cl$	8.5, 9.0, 10.3, 11.0 93.5, 94.9, 98.0, 98.3, 119.0 (t, 4)	−20.0	122.5, 127.8, 133.2, 139.7	173.1	−13.9 (t, 5)	CH_2, 13.4 [m, $^1J(P-C) = {}^3J(P-C) = {}^2J(Pt-C)$ 32 Hz], CH_3, 7.8 [t, $^3J(Pt-C)$ 24 Hz]
	c-$Pt(PEt_3)_2Cl$	8.8, 8.9, 9.7, 10.0 92.2, 94.9, 96.0, 97.3, 118.9(17)	−22.4	121.8, 127.2, 133.2, 140.2	174.9	−13.9 (17)	CH_2, 15.5–16.5m; CH_3, 8.2–8.4m
4a	$SiMe_3$	8.9, 8.9, 9.3, 9.4 93.0, 93.8, 99.2, 99.6, 109.4	−16.6		171.0	14.0	$SiMe_3$, −0.58
4b	CH_2Ph	8.5, 8.5, 8.7 98.5, 98.7, 99.5, 99.8, 100.8	−17.5		170.5	26.3	CH_2Ph, 35.8; Ph, 126.5 C^4 128.6, 128.6 C^{2-3}, 140.2 C^1
4c	$CH_2CH{=}CH_2$	8.5, 8.7, 8.9, 9.0 98.2, 99.3, 99.4, 99.7, 100.7	−17.5		170.6	23.6	$CH_2CH{=}$, 33.8; $CH_2{=}$ 116.1; CH= 136.7
5a	$SiMe_3$	9.3, 9.3 92.8, 100.8, 112.9			167.1	15.1	$SiMe_3$, −0.5

5b	CH_2Ph	9.0 97.8, 100.5, 101.4			166.6	26.4	CH_2, 34.7; Ph, 126.8 C^4, 128.7, 128.8 C^{2-3}, 139.3 C^1
5c	$CH_2CH{=}CH_2$	9.1, 9.4 98.7, 100.2, 101.4			166.6	23.7	CH_2-, 32.7; $CH_2=$, 116.9; $CH=$, 135.8
6a	$SiMe_3$	9.6, 10.3 81.6, 86.7, 96.5				14.5	$SiMe_3$, −0.3
6b	CH_2Ph	9.1, 9.2 86.3, 87.2				26.6	CH_2, 33.6; Ph, 126.3 C^4 128.5, 128.6 $C^{2,3}$, 140.2 C^1
6c	$CH_2CH{=}CH_2$ [a]	7.7, 8.0, 8.8, 9.4 80.6, 87.6, 102.7, 109.3, 115.2				23.9	CH_2, 40.1; $=CH_2$, 64.3; $=CH-$, 96.2
7		8.8, 9.0, 9.4, 9.7 93.7, 94.9, 98.8, 98.9, 104.7	−21.2	122.8, 128.0, 131.3, 139.6	172.7	12.6	$SiMe_2$, −1.2
8		8.2, 8.3, 8.5, 8.6, 8.7, 9.3 86.5(3), 92.2(2) 95.7(8), 98.5(14), 99.7, 101.7, 103.4	21.5	122.7, 127.7, 130.3, 139.5	172.0	CH_2Si 13.3 CH_2P 26.2 (27)	$SiMe_3$, 0.4 Ph_2P, 128.3(49) C^1, 135.4(9) C^2, 127.6(10) C^3, 130.9 C^4
10		9.4, 10.2 88.6, 93.9, 94.2, 109.6, 109.7	−16.1	–	171.2	13.9	$SiMe_3$, −0.5
12a [b]		6.1, 7.0 94.9, 96.7, 104.1	−1.9	–	–	10.9	$SiMe_3$, −1.2
12f [b]		6.1, 6.2 96.8, 98.1, 100.5	−2.9	–	–	24.1	CH_2, 22.1; Me, 14.3

[a] Spectrum in CD_2Cl_2 at −50 °C; at +24 °C signals were only observed at δ 8.7, 9.1 (Me), 25.2, 41.4 (CH_2CH_2). [b] C_6D_6 solution.

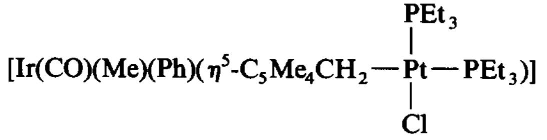
four C_5 ring methyls are diastereotopic, and show four separate signals in both the ^1H (Table 2) and the ^{13}C NMR spectra (Table 3).

Complex [Ir(CO)(Me)(Ph)(η⁵-C₅Me₄CH₂Pt(PEt₃)₂Cl)] (3e)



$$[Ir(CO)(Me)(Ph)(\eta^5\text{-}C_5Me_4CH_2-\overset{PEt_3}{\underset{PEt_3}{Pt}}-Cl)] \rightleftharpoons$$

(**3e**, *trans*)



$$[Ir(CO)(Me)(Ph)(\eta^5\text{-}C_5Me_4CH_2-\overset{PEt_3}{\underset{Cl}{Pt}}-PEt_3)]$$

(**3e**, *cis*)

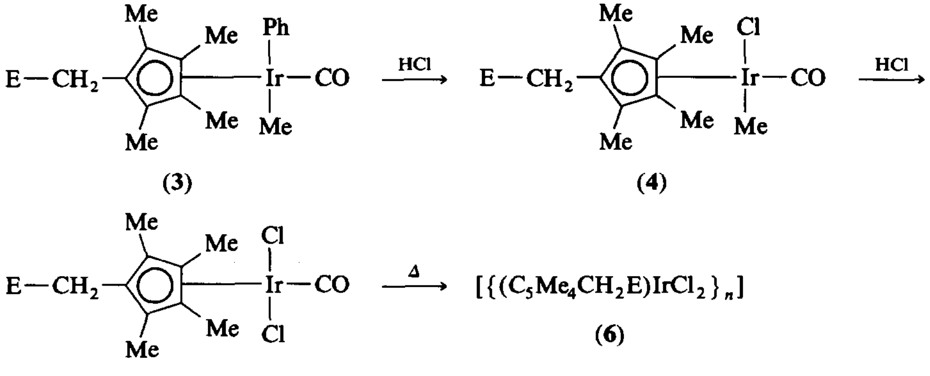
Since **2** reacted readily with a number of simple halides, it was also reacted with *trans*-$Pt(PEt_3)_2Cl_2$. This reaction gave a product, **3e**, in which the $C_5Me_4CH_2$ was bonded to Pt, as can be seen from the coupling of the CH_2 hydrogens to both P and Pt in the ^1H NMR spectrum. This complex can exist in two isomeric forms, with the Et_3P ligands *trans*- or *cis*- about the Pt.

The isomer which is formed initially is hexane soluble and shows a singlet in the ^{31}P NMR spectrum at δ +11.9 ppm, with satellites arising from coupling to ^{195}Pt [$I = 1/2$, 33.8% abundance; J(Pt–P) 2879 Hz], indicative of a *trans*-geometry. On crystallisation from methanol isomerisation occurs to the *cis*-isomer, which is insoluble in hexane. The two Et_3P ligands are now inequivalent and show two ^{31}P resonances [δ + 13.2, J(Pt–P) 4222 Hz; and +7.8, J(Pt–P) 1746 Hz], which also couple to each other, $J(P_a–P_b)$ 16 Hz. The change in stereochemistry is also accompanied by a marked decrease in ν(CO), from the "normal" value of 1989 cm^{-1} in the *trans*-isomer to 1963 cm^{-1} in the *cis*-isomer. This suggests that the iridium back-bonds to the CO more efficiently in the *cis*-isomer and that *cis*-$Pt(PEt_3)_2Cl$ is a better electron donor than the *trans*-form.

Complexes [(C₅Me₄CH₂E)Ir(Me)CO(Cl)] (4), [(C₅Me₄CH₂E)Ir(Cl)₂CO] (5), and [((C₅Me₄CH₂E)IrCl₂)ₙ] (6)

On reaction of the complexes **3a–c** with hydrogen chloride, the Ir–phenyl bond was broken and replaced by Cl, giving the complexes **4a–c**. The change in the formal charge felt by the metal in **4** can be seen from the 15 cm^{-1} increase in ν(CO) to ca 2010 cm^{-1} by comparison to **3**. The other notable difference is that complexes **4** are less lipophilic than **3**, and hence easier to crystallise.

Under more forcing conditions with HCl, complexes **4a–c** are transformed into the dichlorocarbonyls **5a–c**. This is again accompanied by a further and more marked rise of ca 45 cm^{-1} in ν(CO) by comparison to **4a–c**. In addition, while the iridium centre is chiral (with diastereotopic ring methyls) in **4** as well as in **3**, this is not the case in **5** or the last complexes of the series **6**. The dichlorocarbonyls **5a–c** are decarbonylated, although heating to 135 °C *in vacuo* is required to complete the reaction. This allows a route from [$\{C_5Me_5Ir\}_2Cl_4$] to [$\{(C_5Me_4CH_2E)Ir\}_2Cl_4$], complexes which will have many applications.



(3) (4) (5)

[$\{(C_5Me_4CH_2E)IrCl_2\}_n$] (6)

($E = SiMe_3$, **a**; CH_2Ph, **b**; $CH_2CH{=}CH_2$, **c**)

The butenyl complex, [$(C_5Me_4CH_2CH_2CH{=}CH_2)IrCl_2$] (6c)

Perhaps the most interesting of these complexes is **6c** which has a 3-butenyl substituent. An osmometric molecular weight determination showed that it was essentially monomeric in chloroform (found, 479, expected for monomer, 438). Molecular models show that the butenyl double bond is well placed for intramolecular coordination to the iridium, and spectroscopic evidence indicates that, in contrast to the situation in **3c**, **4c**, or **5c**, where there is no vacant coordination site on the metal for the olefin to bind, internal coordination does occur in **6c**. Thus, comparing the ^1H NMR spectra of **6c** with those for **3c**, **4c** and **5c**, we find that the resonances for H^1, H^2, H^3 are close to δ 5.80, 5.02 and 5.00 for **3c**, **4c** and **5c**; in **6c** they come at δ 5.49, 4.32 and 4.58. The shift to higher field (lower frequency) is consistent with a coordination of the double bond to the metal in **6c** but not in the others. The *trans*- and *cis*-coupling constants in **6c**, $J(H^1\text{–}H^2)$ 13, $J(H^1\text{–}H^3)$ 8 Hz, are slightly smaller than those for the uncoordinated olefin (17 and 10 Hz).

The H chemical shift differences between the coordinated and the uncoordinated vinyl are smaller than for related systems ([9], see below); however, the coordination of the double bond in **6c** is clearly shown by the difference in the ^{13}C chemical shifts, δ 135.8 and 116.9 for uncoordinated $CH{=}$ and $=CH_2$ respectively in **5c**, compared to 96.2 and 64.3 for the same atoms in **6c**. Further confirmation comes from the IR spectra: while complex **5c** shows a weak band due to an uncoordinated $\nu(C{=}C)$ at 1620 cm^{-1}, this is absent in **6c**; presumably on coordination the band moves down into a crowded region of the spectrum.

The ^1H vinylic signals of **6c** do not change on cooling the solution. However, changes in the remainder of the spectrum reveal a fluxional process which is slow on the ^1H NMR timescale by −50 °C. At ambient, two singlets are seen for the C_5Me_4 ring methyls; at −50 °C, there are four, thus the ring now reflects an asymmetric situation about the metal. Similarly, the signal at δ 3.11 (due to the allylic CH_2s) is split into two (δ 2.96, 3.26). There is also a smaller and less well-defined change in the ring-CH_2 to which the allyl is attached, at δ 2.51, from a clean triplet at ambient to a multiplet at the lower temperature. The fact that the vinyl signals do not change, but that the ring methyls and the $-CH_2CH_2-$ do, is indicative of a dynamic process involving the $-CH_2CH_2-$ link. A "CH_2-twitch" (a type of racemisation, as illustrated in Scheme 1) would have the effect of appearing to give a plane of symmetry to the C_5 ring. The ^{13}C NMR spectra are consistent with this; they also show dynamic behaviour at ambient temperatures, which is frozen out at −50 °C, where four ring methyls are clearly distinguished.

A number of complexes are known with the metal coordinated to an olefin pendant from an η^5- or η^6-ring [9]. CPK models show that, when the olefin in **6c** is linked by a $-CH_2-CH_2-$ chain to the ring, the olefin can coordinate to the metal either perpendicular or parallel to the plane of the ring. In most of the complexes studied, it has been presumed that the parallel orientation is favoured. This is certainly true for the cobalt(I) complexes $[(C_5Me_4CH_2CH_2CH{=}CH_2)Co(L)]$, derived from $Co_2(CO)_8$ and (3-butenyl)tetramethylcyclopentadiene (L = CO, PR_3, olefin, etc), recently reported by Okuda and Zimmermann [10]. An X-ray structure of the complex with L = $Me_3SiC{\equiv}CSiMe_3$ shows that, as expected for a d^8 $CpML_2$ complex, the butenyl double bond and the acetylene triple bond are parallel to each other and to the plane of the ring. In $[(C_5Me_4CH_2CH_2CH{=}CH_2)Co(L)]$ the vinylic resonances in the NMR spectra are shifted upfield on coordination (but to a greater extent than in **6c**) and $\nu(C{=}C)$, in this case at 1640 cm^{-1} in the IR, is lost on coordination.

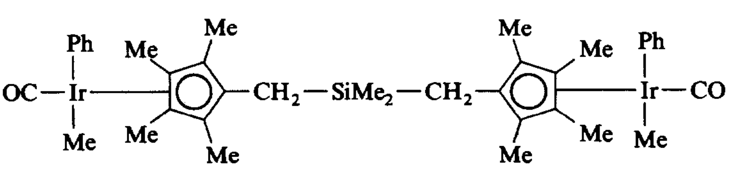
Whether this is also true for **6c** will have to await an X-ray study. The NMR criteria which have been used by some authors [9] seem difficult to justify in all cases because of the lack of definitive examples of parallel and perpendicular bonding with which they may be compared. CPK models suggest that in **6c** the non-bonded repulsions between the ring methyls and the vinylic hydrogens are greater for the parallel than the perpendicular case; there may, however, be electronic factors favouring the other. Scheme 1 illustrates the CH_2-twitch racemisation for (a) the perpendicular, and (b) the parallel arrangement.

Somewhat surprisingly and in contrast to the situation in **6c**, the iodide $[\{(C_5Me_4CH_2CH_2CH{=}CH_2)CoI_2\}_2]$ is dimeric with I-bridges and an uncoordinated butene [10].

Dinuclear complexes

When the lithio-intermediate **2** was reacted with half an equivalent of a dichlorosilane, a dinuclear μ-dimethylsilyl complex **7** was formed,

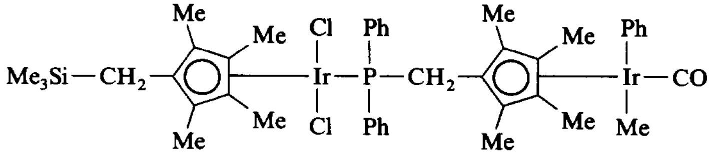
$2\,(\mathbf{2}) + Me_2SiCl_2 \longrightarrow$



(7)

Only one form of **7** is seen in the NMR spectra; this presumably arises from the accidental equivalence of the signals of the *dl*- and *meso*-forms.

Another dinuclear complex, **8**, is formed by reaction of the diphenylphosphine complex **3d**, acting as a ligand this time, with the silylmethylcyclopentadienyl complex **6a** (see below),



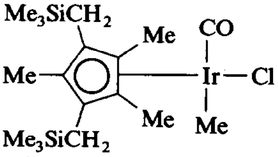
(8)

The structure of **8** comes from the ^1H and ^{13}C NMR spectra; two C_5Me_4 rings are clearly shown, in addition to two different CH_2–C_5Me_4 units, one bound to Si, the other to P. Preliminary data for an X-ray single crystal determination also agree with the structure proposed.

The ring disubstituted complex [($C_5Me_3(CH_2SiMe_3)_2$)Ir(CO)(Me)(Ph)]

The monosubstituted complexes **3** can also be remetallated to give the disubstituted derivatives. Thus, the trimethylsilyl complex **3a** underwent a second reaction with sec-butyllithium, which on reaction with $SiMe_3Cl$ gave the bis(trimethylsilyl) complex, [{$C_5Me_3(CH_2SiMe_3)_2$}Ir(CO)(Me)(Ph)] (**9**). Unfortunately this proved impossible to crystallise and it was therefore converted into the chloromethyl complex [{$C_5Me_3(CH_2SiMe_3)_2$}Ir(CO)(Me)(Cl)] (**10**) by reaction with HCl. The spectroscopic properties of **10** were as expected, and quite similar to those of **4a**, and did not allow a distinction between the two sites for reaction, with the second $SiMe_3$ going either 2- or 3- to the first methyl attacked. Either can be rationalised; if the position of attack of the lithium alkyl on **3a** is determined by steric factors only, then it would be expected to attack as far away from the bulky $SiMe_3$ as possible, i.e., 3- to it. On the other hand, if there was some attractive interaction between the Me_3Si and the attacking alkyllithium, then it should go 2-.

An X-ray structure determination was carried out on **10** which showed the two $SiMe_3$ substituents to be 1,3- (Fig. 1), and thus the metallation indeed goes 3- to the substituent already present. The structure showed the expected three-legged piano-stool geometry with the $C_5Me_3(CH_2SiMe_3)_2$ ring η^5-bonded to the iridium (r.m.s. deviation 0.030 Å, perpendicular displacement 1.874 Å). The three C_5 ring methyls are almost coplanar (displacements < 0.03 Å from the mean C_5 plane, away from the metal), while the two CH_2SiMe_3 substituents are similarly but more bent away (0.18, 0.19 Å). The bonds to the three other ligands on the iridium (Me, Cl, and CO) are at very nearly 90° to each other, and the Me and CO are approximately eclipsed by the CH_2SiMe_3s.



(11)

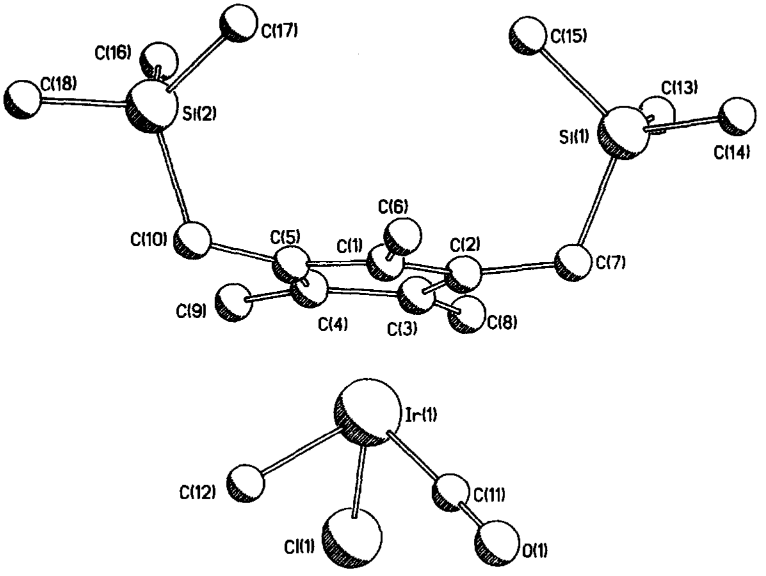
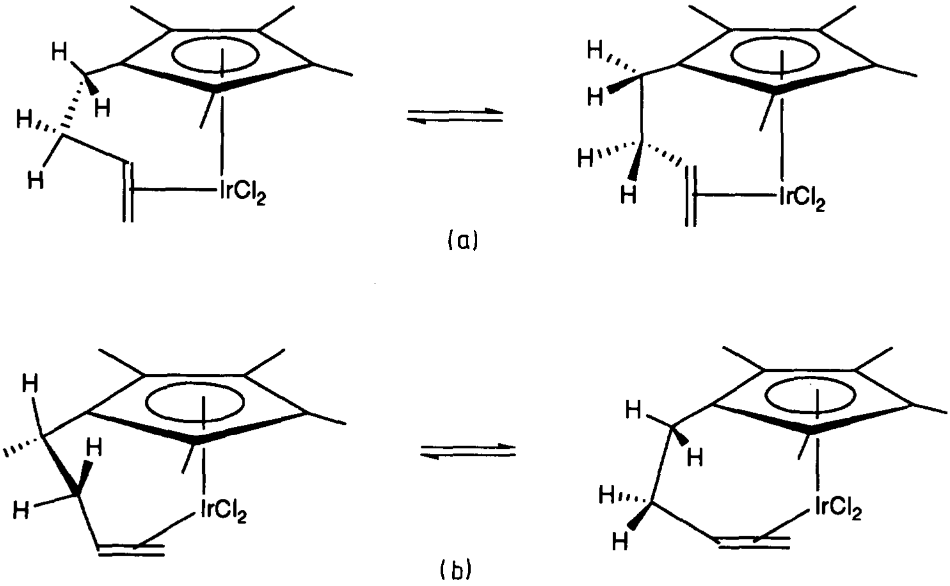


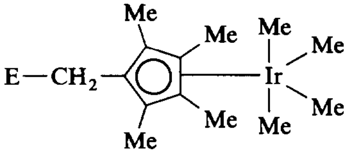
Fig. 1. View of the structure of the bistrimethylsilylmethylene complex [$(C_5Me_3(CH_2SiMe_3)_2)Ir(Me)CO(Cl)$] (**10**).



Scheme 1. Illustration of the "CH_2-twitch" racemisation processes possible for complex **6c**; (a) with olefin perpendicular, and (b) with olefin parallel to the ring plane.

Iridium(V) complexes

We are still in the process of establishing criteria for metallation to occur at C_5Me_5 rings, but we have already found that the iridium(V) tetramethyl complex, $[C_5Me_5IrMe_4]$ (**11**) [11] can also be metallated and substituted on the C_5Me_5 ring, analogously to **1**. In this case the trimethylsilylmethyl and the n-propyl substituents were introduced, to give **12a** and **12f** respectively, in ca 70% yield.



(**12**: **a**, E = $SiMe_3$; **f**, E = CH_3CH_2)

Again here, as in **1**, the ring substitution occurs without change in the formal oxidation state and the products, **12**, are also Ir(V) complexes.

Conclusion

While the activation of methyls on η^6-bonded arene rings is quite common [7], there have, until recently, been very few examples of the activation of methyls on η^5-C_5 rings [5,6]. In view of the utility of C_5 ring complexes of Rh and Ir in various types of catalytic reaction [2] this project was undertaken. We have shown that, under the appropriate conditions, one or more methyls in C_5Me_5Ir (and also, more recently, in C_5Me_5Rh [12]) complexes can be activated and substituted, opening up a substantial new area of chemistry.

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 spectra (PE-1600 FT-IR) are collected in Table 1, ^1H NMR spectra (Bruker AM-250) in Table 2, and ^{13}C NMR spectra (Bruker AM-250) in Table 3. Typical procedures are detailed below; the amount of active sec-butyllithium in the solution was determined by titration [13].

$[(C_5Me_4CH_2SiMe_3)Ir(CO)(Me)(Ph)]$ (3a)

A Schlenk tube (50 cm^3 capacity) containing $[C_5Me_5Ir(CO)(Me)(Ph)]$ (**1**, 0.1 g, 0.223 mmol) [7], a magnetic stirrer, and capped with a Suba-seal, was evacuated and filled with dry nitrogen several times. Dry THF (5 cm^3) was injected and the resultant colourless solution was cooled to $-78\,^\circ C$ (solid CO_2–acetone) under a flow of nitrogen. sec-Butyllithium (280 μL; Aldrich, 1.2 *M* in cyclohexane; Li/Ir ratio 1.5/1) was then injected. The colour changed to yellow. The solution was stirred at $-78\,^\circ C$ (1 h), after which trimethylchlorosilane (42.5 μL; Li/Si ratio 1/1.5) was added; the yellow colour faded immediately. The solution was then allowed to warm up to $20\,^\circ C$, the solvent was removed *in vacuo*, and the residual white solid was extracted with pentane (3×10 cm^3). The solution was filtered, and the solvent removed *in vacuo*. The solid was crystallised from pentane at − 20 ° C to give [($C_5Me_4CH_2SiMe_3$)Ir(CO)(Me)(Ph)] (**3a**), yield, 0.103 g, 89%.

*[($C_5Me_4CH_2SiMe_3$)Ir(CO)(Me)(Cl)] (**4a**)*

A stream of dry hydrogen chloride gas was gently bubbled (4 min) through a stirred solution of [($C_5Me_4CH_2SiMe_3$)Ir(CO)(Me)(Ph)] (**3a**, 0.20 g, 0.385 mmol) in pentane (40 cm^3). The colour turned yellow. Dry nitrogen was then bubbled through to remove excess HCl gas. The solution was dried ($MgSO_4$), filtered, and the solvent removed *in vacuo* to give yellow crystals of [($C_5Me_4CH_2SiMe_3$)Ir(CO)(Me)(Cl)] (**4a**), which were recrystallised from diethyl ether/pentane at −20 ° C, yield 0.164 g, 89%.

*[($C_5Me_4CH_2SiMe_3$)Ir(CO)Cl_2] (**5a**)*

A stream of dry hydrogen chloride gas was gently bubbled (4 min) through a stirred solution of [($C_5Me_4CH_2SiMe_3$)Ir(CO)(Me)(Ph)] (**3a**, 0.15 g, 0.289 mmol) in dichloromethane (20 cm^3). The solution turned yellow and was set aside (24 h/25 ° C). The extent of the reaction was monitored by IR to determine how much [($C_5Me_4CH_2SiMe_3$)Ir(CO)Cl_2] (orange-yellow), ν(CO) 2055 cm^{-1}, had been formed and how much [($C_5Me_4CH_2SiMe_3$)Ir(CO)(Me)(Ph)] (lemon-yellow), ν(CO) 2007 cm^{-1}, still remained. When the reaction had gone to completion, excess HCl gas was removed by bubbling nitrogen gas through the solution; the solution was then dried ($MgSO_4$), filtered, and the solvent removed *in vacuo* to leave an orange-yellow solid which was washed with hexane (3 × 10 cm^3) and crystallised from dichloromethane/hexane to give [($C_5Me_4CH_2SiMe_3$)Ir(CO)Cl_2] (**5a**), yield 0.137 g, 95%.

*[{($C_5Me_4CH_2SiMe_3$)IrCl_2}$_2$] (**6a**)*

A sample of [($C_5Me_4CH_2SiMe_3$)Ir(CO)Cl_2] (**5a**, 0.227 g, mmol) was heated (2 h, 135 ° C) *in vacuo* in a Schlenk tube. The residual solid was extracted with dichloromethane (3 × 5 cm^3), the extracts were combined, and hexane (15 cm^3) added. On concentration on a rotary evaporator, yellow [{($C_5Me_4CH_2SiMe_3$)IrCl_2}$_2$] (**6a**), 0.185 g, 86% was obtained, recrystallised as orange-red crystals from dichloromethane/diethyl ether at −20 ° C.

*[($C_5Me_4CH_2CH_2CH=CH_2$)Ir(CO)(Me)(Ph)] (**3c**)*

[C_5Me_5Ir(CO)(Me)(Ph)] (**1**, 0.16 g, 0.357 mmol), was reacted with sec-butyllithium (450 μL; Aldrich, 1.2 *M* in cyclohexane; Li/Ir ratio 1.5/1; −78 ° C). The colour changed to yellow. Allyl bromide (1-bromoprop-2-ene) (50 μL; Li/Br ratio 1/1.1) was added and the yellow colour disappeared (3 min); after work-up and crystallisation of the resulting oil from methanol (−20 ° C) [($C_5Me_4CH_2CH_2$-$CH=CH_2$)Ir(CO)(Me)(Ph)] (**3c**), yield 0.159 g, 91% was obtained.

*[($C_5Me_4CH_2PPh_2$)Ir(CO)(Me)(Ph)] (**3d**)*

[(C_5Me_5)Ir(CO)(Me)(Ph)] (**1**, 0.3 g, 0.670 mmol) was reacted with sec-butyllithium (670 μL; Aldrich, 1.2 *M* in cyclohexane; Li/Ir ratio 1/1.2) at −78 ° C (1 h), after which freshly distilled diphenylphosphine chloride (120 μL; Ir/P ratio 1/1) was added. The solvent was removed *in vacuo*, and the residual oil–solid was extracted with pentane (4 × 25 cm^3). Chromatography of this extract on neutral alumina (3% deactivated), using first hexane and then hexane/diethyl ether (9/1) as eluant gave a colourless solution. The solvent was removed *in vacuo* and the resultant oil was crystallised from hexane (at $-20\,^\circ C$) to yield **3d**, 0.237 g (56%).

*$[\{C_5Me_4CH_2$-*cis- *and* trans-*$(Pt(PEt_3)_2Cl)\}Ir(CO)(Me)(Ph)]$ (**3e**)*

$[(C_5Me_5)Ir(CO)(Me)(Ph)]$ (**1**, 0.15 g, 0.335 mmol) was reacted with sec-butyllithium (335 μL; Aldrich, 1.2 *M* in cyclohexane; Li/Ir ratio 1/1.2), after which *trans*-$[Pt(PEt_3)_2Cl_2]$ (0.168 g; Ir/Pt ratio 1/1) was added. A conventional work-up was followed by chromatography on neutral alumina (3% deactivated), and crystallisation from hexane at ($-20\,^\circ C$) to give $[\{C_5Me_4CH_2$-*trans*-$(Pt(PEt_3)_2Cl)\}Ir(CO)(Me)(Ph)]$.

When the complex was crystallised from MeOH at $-20\,^\circ C$ the platinum complex isomerised to the *cis*-isomer, which crystallised from dichloromethane/hexane at $-20\,^\circ C$ as white needles (now insoluble in hexane) of $[\{C_5Me_4CH_2$-*cis*-$(Pt(PEt_3)_2Cl)\}Ir(CO)(Me)(Ph)]$.

$[\{(C_5Me_4CH_2)Ir(CO)(Me)(Ph)\}_2SiMe_2]$ (7)

$[(C_5Me_5)Ir(CO)(Me)(Ph)]$ (0.31 g, 0.693 mmol) was reacted with sec-butyllithium (750 μL; Aldrich, 1.2 *M* in cyclohexane; Li/Ir ratio 1/1.3) at $-78\,^\circ C$ (1 h), after which dimethyldichlorosilane (42 μL; Ir/Cl ratio 1/1) was added; the yellow colour faded immediately. After a conventional work-up and chromatography complex **7** was crystallised from pentane at $-20\,^\circ C$. Yield 0.233 g (71%).

*$[\{(C_5Me_4CH_2$-μ-$PPh_2)Ir(CO)(Me)(Ph)\}\{(C_5Me_4CH_2SiMe_3)IrCl_2\}]$ (**8**)*

A solution of complex $[(C_5Me_4CH_2PPh_2)Ir(CO)(Me)(Ph)]$ (**3d**, 0.05 g, 0.08 mmol) and $[\{(C_5Me_4CH_2SiMe_3)Ir\}_2Cl_4]$ (**6a**) (0.037 g, 0.04 mmol) in dichloromethane (5 cm^3) was stirred (24 h/$20\,^\circ C$). The solvent was removed and the residue crystallised from dichloromethane-diethyl ether to yield **8**, 0.065 g.

*$[(C_5Me_3(CH_2SiMe_3)_2)Ir(CO)(Me)(Cl)]$ (**10**)*

$[(C_5Me_4CH_2SiMe_3)Ir(CO)(Me)(Ph)]$ (**3a**, 0.235 g, 0.452 mmol) was reacted with sec-butyllithium (570 μL; Aldrich, 1.2 *M* in cyclohexane; Li/Ir ratio 1/1.5) at $-78\,^\circ C$ (1 h), after which trimethylchlorosilane (105 μL; Li/Si ratio 1/1.2) was added; the yellow colour faded immediately. A conventional work-up and chromatography followed by cooling a solution in pentane at $-20\,^\circ C$ yielded $[\{C_5Me_3(CH_2SiMe_3)_2\}Ir(CO)(Me)(Ph)]$ (**9**), [ν(CO), hexane, 1990 cm^{-1}] as an uncrystallisable oil. A stream of HCl gas was gently bubbled (2 min) through a solution of this oil in dichloromethane (20 cm^3); work-up followed by chromatography on alumina gave yellow crystals of $[\{C_5Me_3(CH_2SiMe_3)_2\}Ir(CO)(Me)(Cl)]$ (**10**), 0.188 g, 76%.

*Crystal structure of $[(\eta^5$-$C_5Me_3(CH_2SiMe_3)_2)Ir(CO)(Me)(Cl)]$ (**10**)*

$C_{18}H_{34}ClIrOSi_2$, $M = 550.28$, crystallised from pentane as yellow square plates. Crystal dimensions $0.35 \times 0.35 \times 0.15$ mm, triclinic, $a = 8.926(9)$, $b = 10.532(18)$, $c = 13.548(21)$ Å, $\alpha = 99.09(13)$, $\beta = 101.64(11)$, $\gamma = 99.42(12)\,^\circ$, $U = 1206(3)$ Å^3; $D_c = 1.515$ g cm^{-3}, $Z = 2$, space group $P\bar{1}$ (C_1^1, no. 2), Mo-K_α radiation ($\lambda = 0.71069$ Å), μ(Mo-K_α) $= 57.25$ cm^{-1}, $F(000) = 543.86$.

Three-dimensional, room temperature X-ray data were collected in the range $3.5 < 2\theta < 50\,^\circ$ on a Nicolet R3 four-circle diffractometer by the omega scan method. The 3157 independent reflections (of 4274 measured) for which $|F|/\sigma(|F|) > 3.0$ were corrected for Lorentz and polarisation effects, and for absorption by analysis of six azimuthal scans (minimum and maximum transmission coefficients 0.174 and 0.262, R_{merge} 0.038). The structure was solved by Patterson and Fourier techniques and refined by blocked cascade least-squares methods. Hydrogen atoms were included in calculated positions, with isotropic thermal parameters related to those of the supporting atom, and refined in riding mode. Refinement converged at a final R 0.0556 (R_w 0.0508, 208 parameters; mean and maximum final Δ/σ 0.005 and 0.017, respectively), with allowance for the thermal anisotropy of all non-hydrogen atoms. A final difference electron density synthesis showed minimum and maximum values of -1.31 and $+1.01$ e Å^{-3}. Complex scattering factors were taken from ref. 14 and from the program package SHELXTL [15] as implemented on the Data General Nova 3 computer. A weighting scheme

Table 4

Bond lengths and angles for the bistrimethylsilylmethylene complex [($C_5Me_3(CH_2SiMe_3)_2$)Ir(Me)CO(Cl)], **10**

(a) Bond lengths (Å)

Ir(1)–Cl(1)	2.392(6)	Ir(1)–C(1)	2.181(11)
Ir(1)–C(2)	2.277(11)	Ir(1)–C(3)	2.256(10)
Ir(1)–C(4)	2.240(11)	Ir(1)–C(5)	2.254(11)
Ir(1)–C(11)	1.848(13)	Ir(1)–C(12)	2.155(12)
Si(1)–C(7)	1.908(12)	Si(1)–C(13)	1.848(12)
Si(1)–C(14)	1.863(15)	Si(1)–C(15)	1.895(15)
Si(2)–C(10)	1.893(12)	Si(2)–C(16)	1.844(14)
Si(2)–C(17)	1.876(21)	Si(2)–C(18)	1.864(13)
O(1)–C(11)	1.164(16)	C(1)–C(2)	1.455(12)
C(1)–C(5)	1.453(15)	C(1)–C(6)	1.512(14)
C(2)–C(3)	1.439(15)	C(2)–C(7)	1.512(16)
C(3)–C(4)	1.464(15)	C(3)–C(8)	1.495(13)
C(4)–C(5)	1.425(13)	C(4)–C(9)	1.515(17)
C(5)–C(10)	1.498(13)		

(b) Bond angles (°)

Cl(1)–Ir(1)–C(11)	91.8(5)	Cl(1)–Ir(1)–C(12)	86.8(5)
C(11)–Ir(1)–C(12)	87.4(5)	C(7)–Si(1)–C(13)	110.2(6)
C(7)–Si(1)–C(14)	108.5(6)	C(13)–Si(1)–C(14)	109.4(6)
C(7)–Si(1)–C(15)	109.8(5)	C(13)–Si(1)–C(15)	109.0(6)
C(14)–Si(1)–C(15)	109.9(7)	C(10)–Si(2)–C(16)	109.0(6)
C(10)–Si(2)–C(17)	111.0(7)	C(16)–Si(2)–C(17)	105.8(8)
C(10)–Si(2)–C(18)	107.5(6)	C(16)–Si(2)–C(18)	111.5(7)
C(17)–Si(2)–C(18)	112.0(8)	C(2)–C(1)–C(5)	108.0(8)
C(2)–C(1)–C(6)	124.8(9)	C(5)–C(1)–C(6)	126.5(8)
C(1)–C(2)–C(3)	107.6(9)	C(1)–C(2)–C(7)	125.2(9)
C(3)–C(2)–C(7)	127.2(8)	C(2)–C(3)–C(4)	107.6(8)
C(2)–C(3)–C(8)	127.0(9)	C(4)–C(3)–C(8)	125.3(9)
C(3)–C(4)–C(5)	108.5(9)	C(3)–C(4)–C(9)	124.3(8)
C(5)–C(4)–C(9)	127.1(9)	C(1)–C(5)–C(4)	107.8(8)
C(1)–C(5)–C(10)	125.8(9)	C(4)–C(5)–C(10)	126.3(10)
Si(1)–C(7)–C(2)	114.9(8)	Si(2)–C(10)–C(5)	116.7(7)
Ir(1)–C(11)–O(1)	175.0(10)		

Table 5

Atomic coordinates ($\times 10^4$) and temperature factors (Å$^2 \times 10^3$) for the bistrimethylsilylmethylene complex $[(C_5Me_3(CH_2SiMe_3)_2)Ir(Me)CO(Cl)]$, **10**

	x	y	z	U_{eq} [a]
Ir(1)	8959(1)	−90(1)	2382(1)	67(1)
Cl(1)	11502(5)	−610(4)	2694(4)	144(2)
Si(1)	7035(4)	2804(3)	5076(2)	75(1)
Si(2)	7149(5)	3344(4)	418(3)	91(2)
O(1)	7503(13)	−2613(10)	2897(8)	137(6)
C(1)	7248(11)	1168(9)	2408(7)	59(4)
C(2)	8188(12)	1431(9)	3457(7)	64(4)
C(3)	9783(11)	1902(11)	3429(7)	68(4)
C(4)	9801(12)	2030(10)	2370(8)	70(4)
C(5)	8242(11)	1638(9)	1760(7)	64(4)
C(6)	5494(13)	701(11)	2102(9)	85(5)
C(7)	7563(14)	1268(10)	4397(8)	77(5)
C(8)	11174(13)	2281(13)	4319(8)	101(6)
C(9)	11253(13)	2548(12)	2022(9)	90(5)
C(10)	7704(14)	1742(10)	660(7)	76(5)
C(11)	8098(15)	−1618(11)	2744(9)	90(6)
C(12)	8579(18)	−1215(11)	848(9)	110(7)
C(13)	8784(16)	3856(12)	5988(10)	119(7)
C(14)	5537(15)	2291(14)	5791(9)	110(7)
C(15)	6229(18)	3766(13)	4094(10)	113(7)
C(16)	8774(22)	4713(13)	1109(11)	157(10)
C(17)	5433(22)	3633(17)	962(12)	163(11)
C(18)	6735(19)	3266(13)	−997(9)	124(8)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalised U_{ij} tensor.

$w^{-1} = [\sigma^2(F) + 0.00063(F)^2]$ was used in the latter stages of refinement. Bond lengths and angles are collected in Table 4; atomic coordinates and temperature factors are in Table 5.

$[(C_5Me_4CH_2CH_2CH_3)IrMe_4]$ (12f)

Complex $[(C_5Me_5)IrMe_4]$ (**11**, 0.100 g, 0.258 mmol) was reacted with sec-butyllithium (260 μL; Aldrich, 1.2 *M* in cyclohexane; Li/Ir ratio 1/1.2; −78 °C). The colour of the solution changed from pale yellow to yellow; on addition of ethyl iodide (30 μL; Li/I 1/1.1) the solution turned pale yellow immediately. After work-up and chromatography (Florisil) pale yellow crystals of $[(C_5Me_4CH_2CH_2CH_3)IrMe_4]$ (**12f**), were obtained, yield 0.071 g (67%).

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