Cyclometallation of Unsaturated Carboxylic Acids by Pentamethylcyclopentadienyl-rhodium and -iridium Complexes. Crystal Structures of $[(C_5Me_5)\overline{Ir(CPh{=}CHCO{-}O})(Me_2SO)]$ and $[(C_5Me_5)\overline{Ir(CPh{=}CHCO}{-}OMe)I]^+$ †

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Reaction of $[(C_5Me_5)MMe_2(Me_2SO)]$ (C_5Me_5 = η-pentamethylcyclopentadienyl) with cinnamic acid gave $[(C_5Me_5)\overline{M(CPh{=}CHCO{-}O})(Me_2SO)]$ (**2**; M = Rh) and (**3a**; M = Ir), while the complexes $[(C_5Me_5)\overline{Ir(CR^1{=}CR^2CO{-}O})(Me_2SO)]$ (**3b**; R^1 = Me, R^2 = H), (**3c**; $R^1 = R^2$ = Me), and (**3d**; R^1 = H, R^2 = Me) were made from the appropriate unsaturated acids. Complex (**3b**) was also made by reaction of $[(C_5Me_5)IrCl_2(Me_2SO)]$ with silver crotonate. Reaction of (**2**), (**3a**), (**3b**), and (**3d**) with methyl iodide gave the complexes $[(C_5Me_5)\overline{M(CR^1{=}CR^2CO}{-}OMe)I]$ (**6**; M = Rh, R^1 = Ph, R^2 = H), (**7a**; M = Ir, R^1 = Ph, R^2 = H), (**7b**; M = Ir, R^1 = Me, R^2 = H), and (**7d**; M = Ir, R^1 = H, R^2 = Me). The complexes were characterised by their n.m.r. spectra and by single crystal *X*-ray determinations for (**3a**) and (**7a**). In each case these showed the presence of a cyclometallated five-membered ring. The MC bonds in (**6**) and (**7**), but not in (**2**) or (**3**), are associated with quite substantial carbenoid character, M=C<. Reaction of (**3a**) or (**3b**) with CO merely caused displacement of the dimethyl sulphoxide to give $[(C_5Me_5)\overline{Ir(CR{=}CHCO{-}O})(CO)]$ (**5**); however, (**7b**) ring-opened with CO to give the σ-alkenyl complex $[(C_5Me_5)Ir(CMe{=}CHCO_2Me)(CO)I]$ (**8**).

Recent papers from this laboratory have reported that cyclometallation of benzoic acid (and of substituted benzoic acids) by C_5Me_5Rh, C_5Me_5Ir, and p-$Me_2CHC_6H_4MeOs$ species proceeds easily to give the appropriate product in 62—91% yields, as for example in equation (1) (C_5Me_5 = η-pentamethylcyclopentadienyl). We have now extended this type of reaction to α,β-unsaturated acids and have made complexes (**2**) and (**3**) by the route (2).

Reactions involving the acrylic acids themselves do not appear to have been previously reported, but related cyclometallations of alkyl methacrylates by $[RuH_2(PPh_3)_4]$,[2] $[MoH_4(dppe)_2]$(dppe = $Ph_2PCH_2CH_2PPh_2$),[3] and $[FeH(dmpe)_2(C_{10}H_7)]$ (dmpe = $Me_2PCH_2CH_2PMe_2$),[4] and of vinyl acetate by $[CuMe(PPh_3)_2]\cdot0.5Et_2O$,[5] have all been carried out [*e.g.*, equation (3)]. Complexes with the similar structural element of the five-membered $\overline{MCCCO}$ ring have been made from acetylenes, including, $[(cp)_2\overline{Ti(CPh{=}CHCO{-}O})]$[6] {from $[(cp)_2TiMe_2]$ (cp = η-C_5H_5) and $PhC{\equiv}CCO_2H$ under hydrogen}, and $[L_2\overline{Ni(CR{=}CRCO{-}O})]$[7] [from a nickel(0) complex, RC_2R, and carbon dioxide].

$$[MoH_4(dppe)_2] + CH_2{=}CMeCO_2R \longrightarrow [\overline{Mo(CH{=}CMeCO}{-}OR)H(dppe)_2] \qquad (3)$$

Results and Discussion

Preparation of the Cyclometallated Substituted Acrylic Acids.—Reactions in the sense of equation (2) were carried out (CH_2Cl_2 solution; 35 °C) between cinnamic acid and the rhodium dimethyl complex (**1a**),[8] or the iridium analogue (**1b**),[8] to give (**2**) (yield 80%) and (**3a**) (76%) respectively. The rhodium complex reacted faster, and the reaction was complete in 16 h, whereas the iridium complex required 48 h to go to completion.

Analogous reactions were carried out between the iridium complex and tiglic acid ($CHMe{=}CMeCO_2H$) or crotonic acid to give (**3c**) (76%) or (**3b**) (70%). In contrast, the same reaction with methacrylic acid gave complex (**3d**) in only 36% yield.

An alternative route (4) was also used to make (**3b**) (78% yield), from the iridium dichloro-complex (**4**). This was quite convenient and did not require (**1b**).

Attempts to make complexes from acrylic acid itself by reaction (2) were all unsuccessful; only polymer was obtained. It therefore appears as if this reaction is rather sensitive to the substituent on the carbon β to the carboxylate group.

The complexes (**2**) and (**3**) were characterised by microanalysis, and spectroscopy (Tables 1—3), and by a single crystal *X*-ray structure determination of (**3a**). The rhodium complex (**2a**) showed a band in the i.r. at 1 614 cm^{-1}, while the iridium complexes showed analogous bands, assigned to ν(CO), at 1 617—1 624 cm^{-1}. The ^1H n.m.r. spectra all showed one peak (15 H) due to the C_5Me_5 ring, two peaks (δ 2.7—3.4) arising from inequivalent Me_2SO methyls, and [except for (**3c**) and (**3d**)] a single vinylic H (δ 6.3—6.7), as well as the resonances for the phenyls or methyls on the cyclometallated rings. The complex (**3d**) from methacrylic acid showed the vinylic H (weakly coupled to the methyl) at δ 7.77. The ^{13}C n.m.r. spectra showed the related features expected; they also showed resonances at δ 182—187 (CO_2), at 126—130 (C–CO_2), and at 152—189 p.p.m. (M–C), due to the three carbons of the cyclometallated ring. The carbon attached to rhodium in (**2**) appears as a doublet at 188.6 p.p.m., J(Rh–C) 29 Hz, due to coupling to ^{103}Rh ($I = \frac{1}{2}$, 100%).

The X-Ray Crystal Structure Determination of $[(C_5Me_5)\overline{Ir(CPh{=}CHCO{-}O})(Me_2SO)]$ (**3a**).—The molecular structure found (Figure 1) comprises an iridium η^5-bonded to a pentamethylcyclopentadienyl ring (perpendicular distance to mean plane, 1.822 Å; methyls displaced by up to 0.13 Å away

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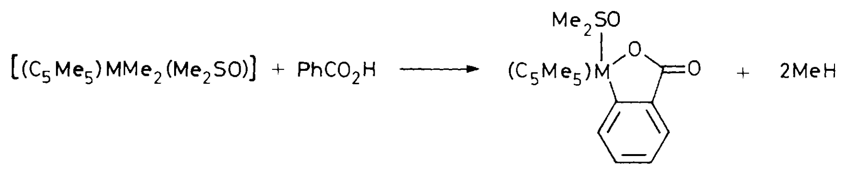
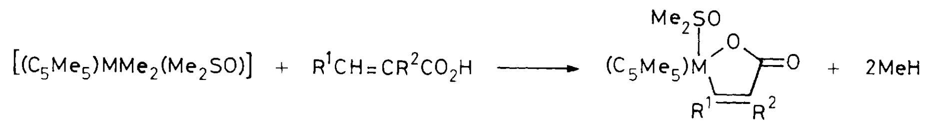
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Non-S.I. unit employed: atm = 101 325 Pa.



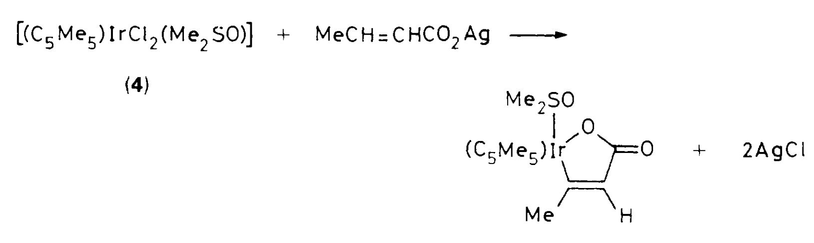
(1)



(2)

(**1a**; M = Rh)
(**1b**; M = Ir)

(**2**, M = Rh, R^1 = Ph, R^2 = H)
(**3a**; M = Ir, R^1 = Ph, R^2 = H)
(**3b**; M = Ir, R^1 = Me, R^2 = H)
(**3c**; M = Ir, R^1 = Me, R^2 = Me)
(**3d**; M = Ir, R^1 = H, R^2 = Me)



(**4**)

(4)

(**3b**)

Table 1. Microanalytical and i.r. spectroscopic data

	Analysis^a (%)					I.r. data (cm^{-1})^b
Complex	C	H	S	I	Yield (%)	ν(CO)
(**2**) $[(C_5Me_5)\overline{Rh(CPh{=}CHCO{-}O})(Me_2SO)]$	54.3 (54.6)	5.9 (5.9)	7.1 (6.9)		80	1 614
(**3a**) $[(C_5Me_5)\overline{Ir(CPh{=}CHCO{-}O})(Me_2SO)]$	45.7 (45.4)	4.9 (4.9)	6.6 (5.8)		76	1 622
(**3b**) $[(C_5Me_5)\overline{Ir(CMe{=}CHCO{-}O})(Me_2SO)]$	39.4 (39.3)	5.4 (5.2)	6.1 (6.6)		78	1 624
(**3c**) $[(C_5Me_5)\overline{Ir(CMe{=}CMeCO{-}O})(Me_2SO)]$	41.0 (40.5)	5.4 (5.4)	6.0 (6.4)		76	1 617
(**3d**) $[(C_5Me_5)\overline{Ir(CH{=}CMeCO{-}O})(Me_2SO)]$	39.2 (39.3)	5.0 (5.2)	6.6 (6.2)		36	1 623
(**5a**) $[(C_5Me_5)\overline{Ir(CPh{=}CHCO{-}O})(CO)]$	47.5 (47.9)	4.4 (4.2)			63	2 022
(**5b**) $[(C_5Me_5)\overline{Ir(CMe{=}CHCO{-}O})(CO)]$	41.8 (41.0)	4.8 (4.4)			72	2 022
(**6**) $[(C_5Me_5)\overline{Rh(CPh{=}CHCO}{-}OMe)I]$	44.0^c (45.6)	4.8 (4.6)		23.8 (24.1)	92	1 581
(**7a**) $[(C_5Me_5)\overline{Ir(CPh{=}CHCO}{-}OMe)I]$	39.2 (39.0)	4.0 (3.9)		20.5 (20.6)	68	1 561
(**7b**) $[(C_5Me_5)\overline{Ir(CMe{=}CHCO}{-}OMe)I]$	32.6 (32.5)	3.9 (4.0)		22.4 (22.9)	82	1 564
(**7b′**) $[(C_5Me_5)\overline{Ir(CMe{=}CHCO}{-}OEt)I]$	35.0 (33.9)	4.6 (4.3)		22.1 (22.4)	84	1 563
(**7d**) $[(C_5Me_5)\overline{Ir(CH{=}CMeCO}{-}OMe)I]$	32.8 (32.5)	4.4 (4.0)		23.4 (22.9)	87	1 583
(**8**) $[(C_5Me_5)Ir(CMe{=}CHCO_2Me)(CO)I]$	33.9 (33.1)	4.0 (3.8)		21.8 (21.8)	86	1 711, 2 036

^{a} Calculated values in parentheses. ^{b} Infrared spectra measured in dichloromethane except for (**6**) and (**7b**) which were measured as a Nujol mull. ^{c} Carbon analysis for this complex is consistently low.

from the metal). The three remaining co-ordination sites of the metal are occupied by (*i*) a S-bonded dimethyl sulphoxide ligand [Ir–S 2.267(9) Å], (*ii*) the carboxylate oxygen of the five-membered cyclometallated ring [Ir–O(2) 2.091(15) Å], and (*iii*) the C-phenyl of the same ring [Ir–C(13) 2.059(17) Å]. These three substituents are very nearly at right angles to each other, as would be expected for an octahedrally co-ordinated Ir [S–Ir–O(2) 88.6(4), S–Ir–C(13) 92.8(5), and C(13)–Ir–O(2) 78.6(6)°]. However, the $\overline{\mathrm{IrCCCO}}$ ring is *not* planar, the iridium being 0.264 Å away from the mean plane of the other atoms [root mean square (r.m.s.) deviation 0.003 Å]. The Ir–C(13) and Ir–O(2) bond lengths are similar to those found in the cyclometallated benzoic acid complex,[1] 2.08 and 2.09 Å respectively. The C(12)–C(13) bond length, 1.33(3) Å, is that for a typical C=C, while that for C(11)–C(12) 1.47(2) Å, is closer to that for a C–C single bond. Thus the canonical form used to

Table 2. ^{1}H N.m.r. spectroscopic data (δ)[a]

Complex	C$_5$Me$_5$	Me$_2$SO	=C–H	OMe	Other
(2) [(C$_5$Me$_5$)Rh(CPhCHCO–O)(Me$_2$SO)]	1.50	2.73 3.22	6.30		Ph, 7.35 (m)
(3a) [(C$_5$Me$_5$)Ir(CPh=CHCO–O)(Me$_2$SO)]	1.55	2.85 3.35	6.66		Ph, 7.30 (m), 7.47 (m)
(3b) [(C$_5$Me$_5$)Ir(CMe=CHCO–O)(Me$_2$SO)]	1.75	2.84 3.15	6.31 (q), (1.5)		Me, 2.48 (d) (1.5)
(3c) [(C$_5$Me$_5$)Ir(CMe=CMeCO–O)(Me$_2$SO)]	1.84	2.70 3.12			Me, 1.75, 2.45 (q) (1)
(3d) [(C$_5$Me$_5$)Ir(CH=CMeCO–O)(Me$_2$SO)]	1.77	2.86 2.99	7.77 (q) (1)		Me, 1.81 (d) (1)
(5a) [(C$_5$Me$_5$)Ir(CPh=CHCO–O)(CO)]	1.69		6.46		Ph, 7.26 (m), 7.33 (m)
(5b) [(C$_5$Me$_5$)Ir(CMe=CHCO–O)(CO)]	2.00		6.20 (q) (1.5)		Me, 2.45 (d) (1.5)
(6) [(C$_5$Me$_5$)Rh(CPh=CHCO–OMe)I]	1.52		6.10 (d) (1)	3.86	Ph, 7.25 (m), 7.75 (m)
(7a) [(C$_5$Me$_5$)Ir(CPh=CHCO–OMe)I]	1.56		6.61	3.94	Ph, 7.28 (m), 7.51 (m)
(7b) [(C$_5$Me$_5$)Ir(CMe=CHCO–OMe)I]	1.78		6.42 (q) (1.5)	3.86	Me, 2.68 (d) (1.5)
(7b′) [(C$_5$Me$_5$)Ir(CMe=CHCO–OEt)I]	1.77		6.42 (q) (1)	OEt, 4.30 (m) 1.30 (t) (7)	Me, 2.78 (d) (1)
(7d) [(C$_5$Me$_5$)Ir(CH=CMeCO–OMe)I]	1.78		9.42 (q) (1)	3.92	Me, 1.90 (d) (1)
(8) [(C$_5$Me$_5$)Ir(CMe=CHCO$_2$Me)(CO)I]	1.99		6.56 (q) (1)	3.65	Me, 2.72 (d) (1)

[a] Coupling J(H–H) in Hz in parentheses. [b] Ethoxy CH$_2$ inequivalent.

Table 3. ^{13}C-{^{1}H} N.m.r. spectroscopic data (δ/p.p.m.)[a]

Complex	C$_5$Me$_5$	Me$_2$SO	CO$_2$	=C–CO$_2$	=C–M	Other
(2) [(C$_5$Me$_5$)Rh(CPh=CHCO–O)(Me$_2$SO)]	8.4 99.5 (d) (6)	42.0 45.1	182.4	128.1[b]	188.6 (d) (29)	Ph, 144.2, 128.0, 127.8, 127.2[b]
(3a) [(C$_5$Me$_5$)Ir(CPh=CHCO–O)(Me$_2$SO)]	8.3 93.9	41.4 45.3	186.7	126.1[b]	173.9	Ph, 144.8, 128.2, 128.0, 127.7[b]
(3b) [(C$_5$Me$_5$)Ir(CMe=CHCO–O)(Me$_2$SO)]	8.8 94.0	42.8 43.9	186.8	126.4	173.1	Me, 28.4
(3c) [(C$_5$Me$_5$)Ir(CMe=CMeCO–O)(Me$_2$SO)]	8.8 93.9	42.9 44.2	186.6	129.7	161.1	Me, 25.8, 15.0
(3d) [(C$_5$Me$_5$)Ir(CH=CMeCO–O)(Me$_2$SO)]	8.5 93.6	41.7 45.0	185.9	136.5	152.4	Me, 20.6
(5a) [(C$_5$Me$_5$)Ir(CPh=CHCO–O)(CO)]	8.6 99.9		186.1	143.7	169.0	CO, 162.1 Ph, 128.2, 128.1, 127.3, 126.7
(5b) [(C$_5$Me$_5$)Ir(CMe=CHCO–O)(CO)]	9.0 99.8		186.2	126.2	168.4	CO, 161.8 Me, 29.2
(6) [(C$_5$Me$_5$)Rh(CPh=CHCO–OMe)I]	9.4 95.8 (d) (6)		179.2	118.0	220.0 (d) (30)	OMe, 53.1 Ph, 147.1, 128.2, 127.7, 127.5
(7a) [(C$_5$Me$_5$)Ir(CPh=CHCO–OMe)I]	9.4 88.5		185.5	116.0	209.0	OMe, 53.6, Ph, 147.8, 128.3, 127.7, 127.5
(7b) [(C$_5$Me$_5$)Ir(CMe=CHCO–OMe)I]	9.9 88.0		N.O.	116.4	211.9	Me, 32.0 OMe, 53.3
(7b′) [(C$_5$Me$_5$)Ir(CMe=CHCO–OEt)I]	9.9 87.9		185.1	116.9	211.3	Me, 14.5 OEt, 62.4, 31.9
(7d) [(C$_5$Me$_5$)Ir(CH=CMeCO–OMe)I]	9.9 87.9		185.0	127.0	187.6	Me, 18.5 OMe, 53.8
(8) [(C$_5$Me$_5$)Ir(CMe=CHCO$_2$Me)(CO)I]	9.7 99.7		166.3[b]	123.7	159.3[b]	OMe, 50.5 Me, 45.2 CO, 167.9[b]

[a] Coupling to ^{103}Rh, J(Rh–C), in Hz in parentheses. [b] Arbitrary assignment.

represent **(3a)** in the formula is a reasonable approximation to the correct situation.

The *X*-ray structure determination showed the presence of a molecule of water in complex **(3a)**. The water H(4A)–O(4)–H(4B) lies between the molecules and is hydrogen-bonded to O(2) of one metallocycle and to O(3′) of the inversion related molecule.

Reaction of [(C$_5$Me$_5$)M(CR=CHCO–O)(Me$_2$SO)] *with* CO *and with* MeI.—The iridium complexes **(3a)** and **(3b)** were treated with CO (toluene/15 h/15 °C/2.5 atm or acetone/2 h/60 °C/1 atm) to give the carbonyl complexes **(5a)** (63%) and **(5b)** (72%); both showed ν(CO) 2 022 cm^{-1}, indicating the presence of a terminal carbonyl group. The ^{1}H and the ^{13}C n.m.r. spectra were consistent with the formulation indicated, and showed that the dimethyl sulphoxide in **(3)** had been replaced by CO.

The complexes **(2a)**, **(3a)**, **(3b)**, and **(3d)** reacted with methyl iodide (2—15 h, 60 °C, toluene) to give adducts, formulated as **(6)**, **(7a)**, **(7b)**, and **(7d)** respectively. The structures of these new

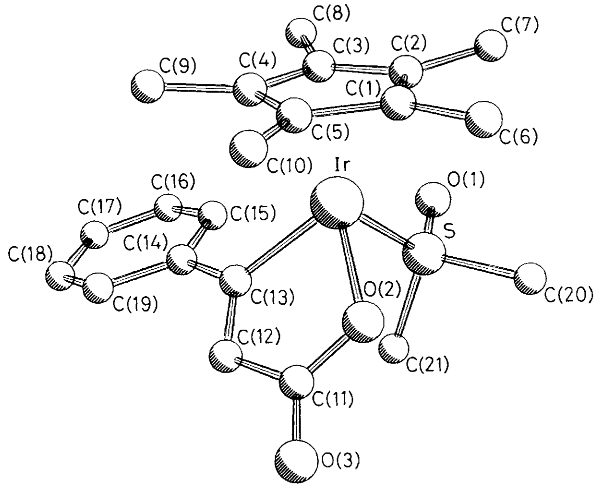
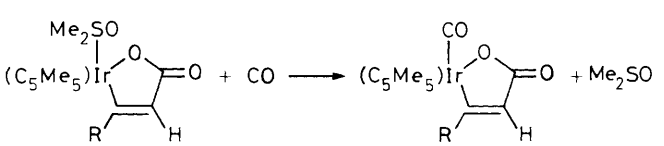
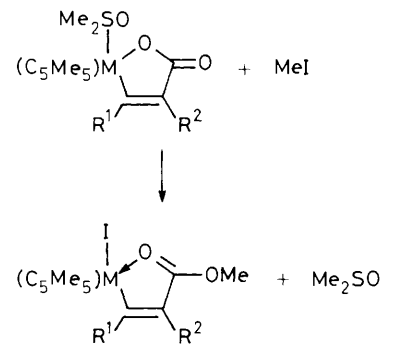


Figure 1. Structure of complex (3a)



(**5a**; R = Ph)

(**5b**; R = Me)



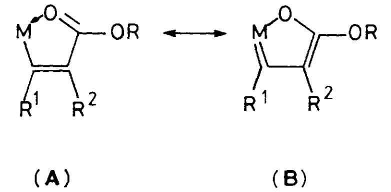
(**6**; M = Rh, R^1 = Ph, R^2 = H)

(**7a**; M = Ir, R^1 = Ph, R^2 = H)

(**7b**; M = Ir, R^1 = Me R^2 = H)

(**7d**; M = Ir, R^1 = H, R^2 = Me)

complexes were assured by their spectra and by an *X*-ray structure determination of (**7a**). The ^1H n.m.r. spectra showed resonances for the C_5Me_5, the cyclometallate C–H, the R group, and, as a new feature, peaks in the region δ 3.65—3.94 characteristic of a methoxy group. There were no resonances due to dimethyl sulphoxide. The ^{13}C n.m.r. spectra were quite consistent with their formulation as (**6**) or (**7**). The rhodium complex (**6**) showed a non-proton-bearing carbon at δ 220 p.p.m., as a doublet arising from coupling to ^{103}Rh, *J*(Rh–C) 30 Hz; this resonance must be assigned to the carbon in the cyclometallated ring attached to rhodium. It contrasts with the same carbon in complex (**2**) which occurs at δ 188.6, 31.4 p.p.m. lower in frequency (Δδ). There are similar marked changes in the position of the carbons in the iridium complexes; thus Δδ is 35.1 between (**3a**) and (**7a**), 38.8 between (**3b**) and (**7b**) and 35.2 p.p.m. between (**3d**) and (**7d**). The region δ 150—175 p.p.m. is quite typical for iridium-alkenyl bonds,[9] and therefore we suggest that the higher resonances seen for (**7**) and (**6**) must be due to substantial contributions from canonical forms (**B**) in which the MC bond now has substantial carbenoid character. By contrast, the canonical form M–CR^1=CR^2 is more important in (**2**) and (**3**).

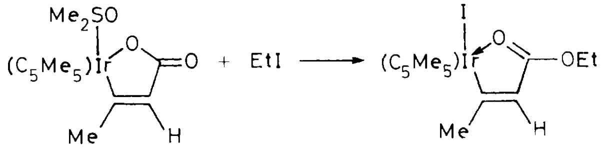


(**A**) (**B**)

Rather similar ideas have been formulated for the structures involved in the molybdenum complexes, [Mo(CH=CMeCO–OR)H(dppe)$_2$][3] and [Mo(CMe=CMeCO–OR)(cp)(CO)$_2$],[10] as well as in the chromium, molybdenum, and tungsten complexes [M(CR^1=CR^{2}CCOR^3)(C_5Me_5)(CO)$_2$].[11]

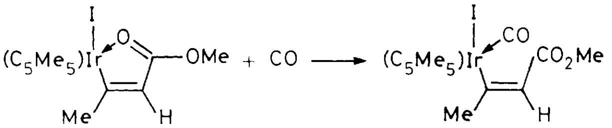
The co-ordination of the ester carbonyl to the metal, or alternatively, the participation of that bond in a delocalised five-membered ring, is also shown by a decrease in ν(CO) from the values of 1 614—1 624 cm^{-1} for (**2**) or (**3**) to 1 561—1 583 cm^{-1} for (**6**) and (**7**).

Complexes (**3**) also react with other alkyl iodides; thus with ethyl iodide complex (**3b**) formed (**7b′**), in an entirely analogous reaction. Complex (**7b′**) was again identified spectroscopically (Tables 1—3); the CH_2 hydrogens were diastereotopic (inequivalent), due to the chiral centre at Ir.



(**3b**) (**7b′**)

While reaction of (**2**) or (**3**) with CO merely displaced the dimethyl sulphoxide by a carbonyl, and no ring opening occurred, when complex (**7b**) was treated with CO the product was the ring-opened complex (**8**). This complex has again been defined spectroscopically; for example the i.r. spectrum shows ν(CO) at 2 036 (Ir–CO) and 1 711 cm^{-1}, typical of an unco-ordinated ester. It is interesting that here the position of the C attached to Ir in the ^{13}C n.m.r. spectrum has dropped right down to *ca.* δ 160, compared to 211.9 in (**7b**), and to 173.1 p.p.m. in (**3b**). This indicates that the carbene-like character of the iridium–alkenyl bond is also highly influenced by the other ligands on the metal, and that such character is best exhibited when the bond can be part of the delocalised ring. This point is also brought home by the *X*-ray crystal structure of (**7a**).



(**7b**) (**8**)

The X-*Ray Crystal Structure Determination of* [(C_5Me_5)Ir(CPh=CHCO–OMe)I] (**7a**).—The molecular

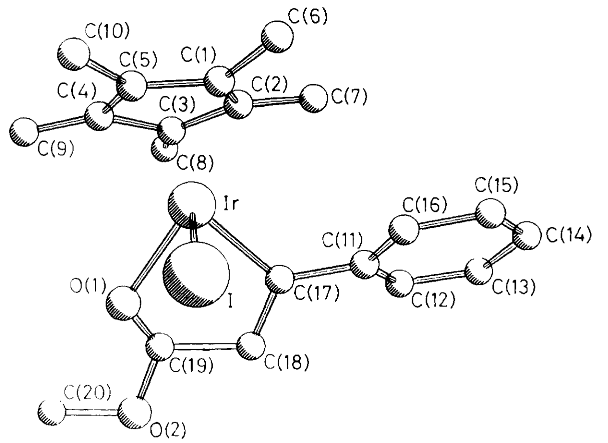


Figure 2. Structure of complex (**7a**)

structure found (Figure 2) comprises an iridium η^5-bonded to a (slightly tilted) pentamethylcyclopentadienyl ring (perpendicular distance to mean plane, 1.797 Å; four of the methyls are displaced away from, and one is bent 0.06 Å towards the metal). The three remaining co-ordination sites of the metal are occupied by (*i*) an iodide [Ir–I 2.681(7) Å], (*ii*) by the oxygen of the cyclometallated five-membered ring [Ir–O(1) 2.151(19) Å], and (*iii*) by the carbon of the same cyclometallated ring [Ir–C(17) 2.026(31) Å]. One marked difference is that the IrCCCO ring in (**7a**) is essentially planar, the iridium lying only 0.035 Å from the mean plane; r.m.s. mean deviation, 0.013 Å. In view of the estimated standard deviations (e.s.d.s) for this determination no quantitative comparison of bond lengths in (**7a**) with those determined above for complex (**3a**) is appropriate; however the changes seen are quite consistent with a longer Ir–O bond in (**7a**) and with some shortening of the Ir–C bond. This supports the conclusion derived from the n.m.r. studies that there is some carbenoid character to the carbon bonded to the Ir.

Experimental

All reactions were carried out in Schlenk tubes, under nitrogen; those involving silver complexes were wrapped in metal foil to retard photochemical decomposition. Typical preparations are described. Microanalyses, carried out by the University of Sheffield Microanalytical Service, and i.r. spectra (PE 1710) are collected in Table 1; Tables 2 and 3 cover the ^{1}H and the ^{13}C n.m.r. spectra of the complexes. N.m.r. spectra were measured in $CDCl_3$ on a Bruker AM-250 spectrometer, except for the ^{13}C n.m.r. spectrum of (**6**) which was measured on a WH-400 spectrometer.

Reaction of $[(C_5Me_5)IrMe_2(Me_2SO)]$ (**1b**) *with Cinnamic Acid.*—Cinnamic acid (0.087 g, 0.59 mmol) and $[(C_5Me_5)IrMe_2(Me_2SO)]$ (0.256 g, 0.59 mmol) were dissolved in dichloromethane (10 cm^3) under nitrogen. The resultant yellow solution was heated (48 h/35 °C). The solvent was then removed on a rotary evaporator and the resultant oil triturated in n-pentane (50 cm^3) to give a yellow powder which was washed with a small amount of diethyl ether (3 cm^3). Yield of $[(C_5Me_5)Ir(CPh{=}CHCO{-}O)(Me_2SO)]$ (**3a**) (0.248 g, 76%).

Reaction of $[(C_5Me_5)IrCl_2(Me_2SO)]$ (**4**) *with Silver Crotonate.*—The complex $[(C_5Me_5)IrCl_2(Me_2SO)]$ (0.495 g, 1.04 mmol) was dissolved in acetone (50 cm^3), under nitrogen and silver crotonate (0.403 g, 2.08 mmol) added. The resultant orange solution/off-white suspension was stirred (24 h/20 °C) producing a yellow solution. The precipitated silver chloride was removed by filtering through Kieselguhr, and the solvent removed *in vacuo* to give an oil. This oil was triturated in n-pentane and washed with n-pentane to give a yellow powder of $[(C_5Me_5)Ir(CMe{=}CHCO{-}O)(Me_2SO)]$ (**3b**) (0.399 g, 78%). (Silver crotonate was prepared by reaction of crotonic acid with 1 equivalent of silver carbonate in acetone. The resultant off-white precipitate was washed with ether and then dried.)

Reaction of $[(C_5Me_5)Ir(CMe{=}CHCO{-}O)(Me_2SO)]$ (**3b**) *with Carbon Monoxide.*—The complex $[(C_5Me_5)Ir(CMe{=}CHCO{-}O)(Me_2SO)]$ (0.150 g, 0.31 mmol) was placed in a thick-walled pressure tube together with a magnetic follower. Toluene (10 cm^3) was added. The pale yellow suspension was stirred under carbon monoxide (20 h/2.5 atm/15 °C). The toluene was removed on a rotary evaporator and the product was dissolved in dichloromethane (3 cm^3) and chromatographed on a short (10 cm) column of alumina. The desired product only eluted with methanol. The solution was evaporated and the solid residue redissolved in dichloromethane (*ca.* 20 cm^3) and treated with anhydrous sodium sulphate (2 g) and activated charcoal (1 g), filtered through Kieselguhr (2 g). After the solvent was removed, the resultant yellow oil was triturated in n-pentane to give a very pale yellow powder of complex (**5b**) (yield 0.098 g, 72%).

Reaction of $[(C_5Me_5)Ir(CMe{=}CHCO{-}O)(Me_2SO)]$ (**3b**) *with Methyl Iodide.*—The complex $[(C_5Me_5)Ir(CMe{=}CHCO{-}O)(Me_2SO)]$ (0.210 g, 0.43 mmol) was placed in a Schlenk tube under nitrogen and toluene (10 cm^3, dry, degassed) added to give a yellow solution/suspension. Methyl iodide (2 cm^3, 32 mmol) was then added and the solution stirred (60 °C/15 h); the solution turned orange very quickly (in less than 10 min) and the remaining precipitate dissolved at this temperature. The solvent and Me_2SO were removed *in vacuo* and the resultant orange residue crystallised from hot n-hexane to give orange microcrystals of $[(C_5Me_5)Ir(CMe{=}CHCO{-}OMe)I]$ (**7b**). Yield 0.196 g (82%).

Reaction of $[(C_5Me_5)Ir(CMe{=}CHCO{-}OMe)I]$ (**7b**) *with Carbon Monoxide.*—The complex $[(C_5Me_5)Ir(CMe{=}CHCO{-}OMe)I]$ (0.095 mg, 0.17 mmol) was dissolved in acetone (80 cm^3) and a smooth stream of carbon monoxide passed through the solution (3 h/50 °C; then 3 h/60 °C). The solvent was then removed *in vacuo* to give pale orange crystals which were dissolved in ether and the solution treated with anhydrous Na_2SO_4 and activated charcoal. The solution was filtered and the ether removed *in vacuo* to give pale orange crystals of $[(C_5Me_5)Ir(CMe){=}CHCO_2Me)(CO)I]$ (**8**) (0.085 g, 86%). The product contained *ca.* 5% of starting material.

X-Ray Structures.—Crystal data for $[(C_5Me_5)Ir(CPh{=}CHCO{-}O)(Me_2SO)]\cdot H_2O$ (**3a**). $C_{21}H_{29}IrO_4S$, M = 569.72, crystallised from CH_2Cl_2–n-hexane as yellow plates, crystal dimensions 0.60 × 0.40 × 0.20 mm, triclinic, a = 8.321(26), b = 9.088(28), c = 16.86(7) Å, α = 73.07(26), β = 84.80(28), γ = 62.51(20)°, U = 1 081(6) Å^3, D_c = 1.751 g cm^{-3}, Z = 2, space group $P\bar{1}$ (C_i, no. 2), Mo-K_α radiation ($\bar{\lambda}$ = 0.710 69 Å), μ(Mo-K_α) = 62.68 cm^{-1}, $F(000)$ = 559.86.

Three-dimensional, room-temperature *X*-ray diffraction data were collected in the range $3.5 < 2\theta < 50°$ on a Nicolet R3 diffractometer by the omega scan method. The 2 724 independent reflections (of 3 821 measured in hemisphere $+h, \pm k, \pm l$) for which $|F|/\sigma(|F|) > 3.0$ were corrected for Lorentz and polarisation effects, and for absorption by analysis of ten azimuthal scans (minimum and maximum transmission

Table 4. Atom co-ordinates (× 10^4) for complex (**3a**)

Atom	*x*	*y*	*z*
Ir	1 900(1)	1 195(1)	2 199(1)
S	2 482(6)	3 452(5)	1 557(3)
O(1)	3 542(17)	3 815(14)	2 065(7)
O(2)	612(14)	1 601(14)	1 091(7)
O(3)	−2 097(16)	2 557(15)	488(7)
O(4)	2 002(21)	517(17)	−393(9)
C(1)	4 059(23)	−1 428(20)	2 240(11)
C(2)	4 757(27)	−691(23)	2 642(11)
C(3)	3 656(29)	−230(24)	3 329(12)
C(4)	2 271(28)	−803(21)	3 355(11)
C(5)	2 487(26)	−1 511(20)	2 686(11)
C(6)	4 822(33)	−2 103(24)	1 506(14)
C(7)	6 471(29)	−452(31)	2 437(16)
C(8)	4 018(40)	455(32)	3 980(15)
C(9)	856(35)	−807(26)	3 992(15)
C(10)	1 438(31)	−2 314(25)	2 448(16)
C(11)	−1 132(24)	2 379(17)	1 078(10)
C(12)	−1 905(22)	3 038(18)	1 795(9)
C(13)	−754(24)	2 792(17)	2 373(9)
C(14)	−1 380(25)	3 586(20)	3 065(10)
C(15)	−295(27)	4 068(21)	3 423(10)
C(16)	−1 015(37)	4 988(24)	4 015(12)
C(17)	−2 727(37)	5 317(30)	4 298(12)
C(18)	−3 776(30)	4 832(26)	3 962(11)
C(19)	−3 132(27)	3 923(21)	3 388(10)
C(20)	3 667(25)	3 117(23)	640(10)
C(21)	526(25)	5 402(20)	1 132(11)

Table 5. Selected bond lengths (Å) and angles (°) for complex (**3a**)

Ir–S	2.267(9)	Ir–O(2)	2.091(15)
Ir–C(1)	2.211(16)	Ir–C(2)	2.228(19)
Ir–C(3)	2.182(20)	Ir–C(4)	2.172(18)
Ir–C(5)	2.179(19)	Ir–C(13)	2.059(17)
S–O(1)	1.480(18)	S–C(20)	1.783(19)
S–C(21)	1.764(15)	O(2)–C(11)	1.287(21)
C(12)–C(13)	1.327(27)	C(11)–C(12)	1.469(24)
O(3)–C(11)	1.262(24)		
S–Ir–O(2)	88.6(4)	S–Ir–C(13)	92.8(5)
O(2)–Ir–C(13)	78.6(6)	Ir–S–O(1)	115.5(5)
Ir–C(20)	110.3(8)	O(1)–S–C(20)	107.6(10)
Ir–S–C(21)	113.9(8)	O(1)–S–C(21)	107.9(9)
C(20)–S–C(21)	100.4(8)	Ir–O(2)–C(11)	114.6(11)
Ir–C(13)–C(14)	125.4(13)	Ir–C(13)–C(12)	112.9(12)

factors 0.205 and 0.337 respectively). The structure was solved by standard Patterson and Fourier techniques and refined by blocked-cascade least-squares methods. Hydrogen atoms were placed in calculated positions with isotropic thermal vibrational parameters related to those of the supporting atom. The refinement converged at a final *R* 0.0592 with allowance for anisotropic thermal motion of all non-hydrogen atoms. Complex scattering factors were taken from ref. 12 and from the SHELXTL program package[13] which was used for the refinement. Unit weights were used throughout the refinement and gave satisfactory convergence. Table 4 lists the atomic co-ordinates for complex (**3a**) and selected bond lengths and angles are presented in Table 5.

Crystal data for $[(C_5Me_5)\overline{Ir(CPh{=}CHCO}{-}OMe)I]$ (**7a**). $C_{20}H_{24}IIrO_2$, $M = 615.51$, crystallised from hot n-heptane as pale orange bricks, crystal dimensions 0.70 × 0.40 × 0.30 mm, orthorhombic, $a = 16.696(38)$, $b = 14.654(25)$, $c = 16.74(5)$ Å, $U = 4\,095(17)$ Å^3, $D_c = 1.997$ g cm^{-3}, $Z = 8$, space group *Pbca* ($D_{2h}{}^{15}$, no. 61); Mo-K_α radiation ($\bar{\lambda} = 0.710\,69$ Å), μ(Mo-K_α) = 79.97 cm^{-1}, $F(000) = 2\,319.47$.

Table 6. Atom co-ordinates (× 10^4) for complex (**7a**)

Atom	*x*	*y*	*z*
Ir	1 871(1)	1 953(1)	2 206(1)
I	2 012(1)	578(2)	3 252(1)
O(1)	806(11)	1 329(13)	1 731(11)
O(2)	389(11)	355(15)	774(12)
C(1)	2 572(7)	2 967(19)	2 818(7)
C(2)	2 555(7)	3 140(18)	1 964(9)
C(3)	1 718(9)	3 309(19)	1 781(8)
C(4)	1 198(7)	3 257(18)	2 474(8)
C(5)	1 761(13)	3 090(19)	3 117(14)
C(6)	3 329(16)	2 824(22)	3 294(20)
C(7)	3 276(18)	3 232(24)	1 432(20)
C(8)	1 359(22)	3 555(26)	983(20)
C(9)	308(17)	3 371(27)	2 516(28)
C(10)	1 496(19)	3 039(22)	3 976(13)
C(11)	3 215(16)	1 076(18)	1 146(13)
C(12)	3 456(16)	1 055(20)	366(15)
C(13)	4 239(18)	1 034(25)	153(21)
C(14)	4 832(20)	997(22)	746(18)
C(15)	4 564(16)	977(25)	1 529(22)
C(16)	3 787(15)	1 028(18)	1 752(16)
C(17)	2 339(18)	1 146(22)	1 341(17)
C(18)	1 714(19)	669(17)	914(13)
C(19)	932(15)	821(17)	1 212(17)
C(20)	−408(17)	648(30)	979(23)

Table 7. Selected bond lengths (Å) and angles (°) in complex (**7a**)

Ir–I	2.681(7)	Ir–O(1)	2.151(19)
Ir–C(1)	2.151(22)	Ir–C(2)	2.119(24)
Ir–C(3)	2.126(28)	Ir–C(4)	2.261(24)
Ir–C(5)	2.266(26)	Ir–C(17)	2.026(31)
I–Ir–O(1)	89.7(5)	I–Ir–C(17)	89.6(9)
O(1)–Ir–C(7)	78.8(10)	Ir–O(1)–C(19)	113.6(17)

Three-dimensional, room-temperature *X*-ray diffraction data were collected in the range $3.5 < 2\theta < 50°$ on a Nicolet R3 diffractometer by the omega scan method. The 2 154 independent reflections (of 4 046 measured in the octant $+h, +k, +l$) for which $|F|/\sigma(|F|) > 3.0$ were corrected for Lorentz and polarisation effects, and for absorption by the analysis of ten azimuthal scans (minimum and maximum transmission factors 0.010 and 0.025 respectively). The structure was solved by Patterson and Fourier techniques and refined by blocked-cascade least-squares methods. Hydrogen atoms were placed in calculated positions with isotropic thermal vibrational parameters related to those of the supporting carbon atoms. The refinement converged at a final *R* 0.0813 with allowance for thermal anisotropy of all non-hydrogen atoms. Complex scattering factors were taken from ref. 12 and from the SHELXTL program package[13] which was used for the refinement. Unit weights were used throughout the refinement and produced satisfactory convergence. Table 6 lists the atomic co-ordinates for (**7a**); selected bond lengths and angles are presented in Table 7.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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